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HYDROGEN IONS

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IN PURE AND INDUSTRIAL CHEMISTRY

BY

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BEING VOLUME THREE OF A SERIES OF
MONOGRAPHS ON APPLIED CHEMISTRY

Under the Editorship of
E. HOWARD TRIPP, Ph.D.

EDITORIAL PREFACE.

In these days of intensive and extensive research, every worker
in science or its applications knows how rapidly the contents of
text-books and encyclopædias become out of date ; and those
who wish to see new work published know the difficulties which
abnormal taxation and high labour costs offer to the realisation
of their desire. The one obvious solution of the problem is the
publication of monographs that would focus attention upon
recent work, or upon new aspects of old work, and upon their
theoretical implications. Such books are usually written by
experts for other experts in related fields of science, or for the
well-educated layman whose thirst for new knowledge has not
been quenched by the more sensuous outpourings of the
ephemeral press.

It is interesting at times to speculate upon what aspects of
our civilisation the future historian will select as the most
characteristic of our time. Scientific discoveries and their
application to human welfare, we may be sure, will find a place ;
and to these many will add the growth of our sense of " values."
The value of new work in science varies greatly : the golden
grain is always accompanied by chaff, and there is no precious
ore without country rock. Owing to the difficulty of assessing
the value of work at the time of its production, we find that our
scientific periodicals stand in danger of being swamped by the
mass of second- and third-rate material that is thought to be
worth publishing, but which posterity will decree would have
been better left in manuscript form. It is the first duty of the
monograph writer to estimate the value, either actual or potential,

of recent work upon the subject of which he writes : he must pick out the plums to save others from the indigestion that follows eating the whole pie. Further, in addition to being accurate, his work must be presented in a form that is both assimilable and attractive ; in other words, he must show that lucid exposition can be achieved by the use of few words, if they are rightly chosen, and that attractive presentation is attained rather by clear thinking than by superficial display.

The present series of monographs has been designed with these objects and ideals in view. The task which the authors have been set is no easy one ; so that should performance occasionally fall short of intention, the critical reader is asked to echo the words of Goethe that " higher aims, even if unfulfilled are in themselves more valuable than lower aims quite attained."

E. HOWARD TRIPP.

AUTHOR'S PREFACE.

HYDROGEN-ION concentrations have long been recognised as an essential factor in many biochemical processes, and it is undoubtedly on account of this recognition that considerable additions have been made in recent years to our knowledge of biochemical principles. In other branches of chemistry, hydrogen-ion concentrations are only just beginning to be regarded as being of fundamental importance, and the use of the hydrogen electrode and the other associated methods are being increasingly applied, not only to measure very small changes in acidity and alkalinity, but as valuable indicators of the extents to which reactions have proceeded and as means of controlling these reactions with an exactitude hitherto impossible. This also applies to various manufacturing processes.

In writing this book the author has endeavoured : firstly, to provide a practical discussion of the various electrometric and colorimetric methods of determining the concentration of hydrogen-ions ; secondly, to show the fundamental importance of hydrogen-ion concentrations in general chemistry, including volumetric and gravimetric analytical procedures ; and finally, to indicate the important rôles played by hydrogen-ion concentrations in numerous industrial chemical processes, and how the various methods of measuring hydrogen-ion concentrations have been employed for the purpose of control. In order to elucidate the importance of hydrogen-ion concentrations in manufacturing processes to the general reader, brief outlines of the processes have been included wherever they were considered necessary.

Methods of very limited application of determining concentrations of hydrogen-ions, such as those depending on the rate of catalytic decompositions, and conductivity measurements have been excluded, in view of the marked superiority of the methods described in the book.

As is well known much controversy is taking place as to the mode of ionisation of strong electrolytes. Unfortunately, the degree of ionisation, if considered in terms of the *concentration* of ions, leads to one standard with which electrode potentials are compared, whereas, if considered in terms of the *activity* of ions it leads to a slightly different standard. In view of there being no really satisfactory theory of solutions incorporating their many properties, the author has deemed it advisable to adhere to the more usual ion-concentration theory in the interpretation of electrode potentials. Discussions of the theories of G. N. Lewis and Debye and Hückel have been considered to be outside the scope of this book, and they should be sought in treatises on physical chemistry or in the original literature. Whatever may be the true interpretations of the potentials of the hydrogen electrode, and of the other electrodes which have been standardised against it, one thing is certain that the voltages constitute a remarkable and delicate means of registering and controlling acidity and alkalinity.

The author gratefully acknowledges his indebtedness to Mr. A. G. Pollard, B.Sc., A.R.C.S., D.I.C., Lecturer in Agricultural Chemistry in the Imperial College of Science and Technology (Royal College of Science), London, for writing the greater portion of Chapter XXX on the " Fertility of Soils " ; a subject on which he and his students have been actively carrying out research for the past few years. The author's best thanks are also due to the Editor of *The Industrial Chemist*, for kind permission to reproduce much of the material contained in Chapters XIX-XXII, XXIV-XXVI, XXVIII, and for the use of the appropriate blocks of the diagrams, which first appeared in the author's articles in that invaluable journal ; to the Chemical Society for kind permission to reproduce several of the diagrams which were

published in the author's original papers in the Society's Journal ; and to Messrs. A. Gallenkamp & Co., Ltd., London, Messrs. Cambridge Instrument Co., Ltd., London, Messrs. The British Drug Houses, Ltd., London, and Messrs. La Motte Chemical Products Co., Baltimore, U.S.A., for the loan of blocks.

In conclusion the author wishes to record his warmest appreciation of the willing and unfailing help accorded him by Mr. F. W. Clifford, F.L.A., Librarian to the Chemical Society, and his able colleagues in the task of searching the extensive literature ; and to thank Dr. E. Howard Tripp Editor of the series of Industrial Monographs, and Mr. W. L. German, B.Sc., University College, Exeter, for their assistance in the reading of the proofs and for valuable criticisms ; and Messrs. Chapman & Hall, Ltd., for undertaking the publication of the book, and for the great care they have taken in its production.

H. T. S. BRITTON.

University College of the South-West of England,
Exeter, *June*, 1929.

CONTENTS.

CHAPTER I.

THEORY OF ELECTROMETRIC METHODS FOR THE DETERMINATION OF HYDROGEN-ION CONCENTRATIONS.

THE increasing recognition of the rôle played by small variations of acidity or alkalinity in reactions, many of which are of technical importance, necessitates an increased attention being directed to those methods by which these factors may be accurately measured and controlled. The considerable effect which very minute changes may have on a reaction render such terms as " slightly acid " or " slightly alkaline " vague and without real meaning. Thus the concentration or " activity " of hydrogen-ions is of fundamental importance in processes which involve the proteins, such as the manufacture of artificial milk foods, leather tanning, the manufacture of glue and gelatin, wool and silk industries, bread making, and many of the fermentation processes connected with brewing, tea-curing, and the ageing of wines and spirits. Although the enzymes, which enter into the fermentation reactions, are usually active to differing extents over wide ranges of acidity, it generally happens that maximum yields can only be obtained by restricting the acidity to relatively narrow ranges.

The productivity of soils often depends upon the hydrogen-ion concentrations which their constituents impart to the " soil solutions "—solutions which are too acid or, in exceptional cases, too alkaline, being poisonous to most plants, and too alkaline solutions render any phosphate which the soil may contain inaccessible to the plant. From a knowledge of the hydrogen-ion concentration, many of the defects of soils can be remedied by the judicious application of lime and suitable fertilisers. By the careful adjustment of hydrogen-ion concentrations, water can be softened, cane and beet-sugar juices can be purified, metallic hydroxides and certain insoluble salts can be separated, certain metallic salts can be prepared, sludges can be precipitated, colloidal emulsions can be broken down, colloidal suspensions of clay can be flocculated, electro-plating can be efficiently carried out, pure metals electrolytically deposited, and many operations which depend upon interfacial forces made satisfactory.

The first chapters deal with the potentiometric methods of determining the concentration or activity of hydrogen-ions, and more especially the use of the hydrogen electrode, for it is with the voltages produced between this electrode, when immersed in different solutions, and some standard electrode, that the quin-hydrone electrode, now often used, the oxygen electrode, various metal-metallic oxide electrodes, the glass electrode, and the colori-metric changes of indicators have been calibrated.   Although the expression " hydrogen-ion concentration " has gained an almost universal usage, it is extremely doubtful what exactly is the true significance of the potential difference set up between a hydrogen electrode and a solution.   This, however, does not detract from the usefulness of the electrode in studying and controlling reactions.   When reactions are carried out in very dilute solutions, there is little doubt that the electromotive force measurements do furnish a satisfactory approximate measure of the concentration of hydrogen-ions.

Theory of Solutions.

Before describing the electrometric methods, it will be an advantage if we review the modern theory of solutions, for it constitutes the basis upon which E.M.F. data are interpreted in terms of ion-concentrations and sometimes of so-called " activities."   Substances on dissolution in water affect to differing extents both the boiling- and freezing-points and vapour pressures of the solutions.   The amounts by which these physical properties are changed can in the case of very dilute solutions of non-electrolytes be shown to be due to the osmotic pressures exerted by the solutes when considered in regard to their molecular concentrations. Now van't Hoff showed that for very dilute solutions of non-electrolytes the Laws of Boyle, Charles, and Avogadro which govern the behaviour of perfect or ideal gases hold almost quantitatively if the osmotic pressure exerted by the solute molecules be substituted for the ordinary gas pressure.   These three laws may be incorporated in the expression

$$PV = xRT,$$

in which P is the osmotic pressure, instead of gaseous pressure, V the volume occupied by the solution containing x gram-molecules of solute, T the temperature in degrees on the Absolute scale of temperature, and R the gas constant.   The value assumed by R is the same for gases and dilute solutions under analogous conditions and when the various factors are measured in the same

units. For use in electrometric calculations we shall evaluate it in terms of the centimetre, gram and second or C.G.S. units. According to Berthelot 1 gm. mol. of a perfect gas occupied in 1904 in the latitude of 45° at 0° C. and under a pressure of one atmosphere, equal to the pressure on each square centimetre of the weight of a column of mercury 76 cm. in height, a volume of 22,412 $\pm$ 2 c.c. The acceleration due to gravity in that year and latitude was 980·665 cm. per second, and therefore 76 cm. of mercury pressure, the specific gravity of mercury being 13·5945, corresponded in C.G.S. units to a force pressing downwards on 1 sq. cm. equal to

$$76 \times 13\cdot5945 \times 980\cdot665 \text{ dynes}$$
$$= 1,013,276 \text{ dynes.}$$

If this value, together with the volume occupied by 1 gm. mol. of gas at 273° A., be substituted in the above expression, we find that

$$R = \frac{P \times V}{x \times T} = \frac{1013276 \times 22412}{1 \times 273}$$
$$= 8\cdot315 \times 10^7 \text{ C.G.S. units or ergs per } 1° \text{ Absolute}$$
$$= 8\cdot315 \text{ joules per } 1° \text{ Absolute } (10^7 \text{ ergs} = 1 \text{ joule}).$$

It happens, however, that the unit of work, *the joule*, involved in this calculation is not quite equal to the amount of work which has been accepted as the practical unit of work, and known as the *international joule*. The relationship between the absolute value of the joule and the international value is that 1 absolute joule is equal to 0·99966 international joule. It will be seen from text-books on physics that electrical work is the product of the quantity of electricity and the E.M.F. which caused the transference of the electricity, in other words, it is equal to E volts $\times$ C ampères $\times t$ seconds, C $\times t$ being the quantity of electricity expressed in ampère-seconds or coulombs. The unit of electrical work is thus seen to be that done when a current of 1 ampère flows for 1 second by means of an E.M.F. equal to 1 volt. Such a unit of electrical work is the joule. Now it happens that both the ampère and volt are referred to the international standard, and consequently in our calculations it will be necessary to convert R into international joules. Hence

$$R = 8\cdot315 \text{ absolute joules per } 1° \text{ Absolute}$$
$$= 8\cdot313 \text{ international joules per } 1° \text{ Absolute.}$$

Van't Hoff found when dilute solutions of electrolytes, namely, solutes which gave the solution the power to conduct the electric current, were considered, that the perfect gas laws were no longer

applicable. The solutions appeared to contain more osmotically active substances than there were molecules of solute. He, however, introduced a factor, i, now usually referred to as the van't Hoff factor, to indicate the relationship between the number of osmotically active substances and the number of molecules of electrolyte in the solution, *i.e.*,

$$i = \frac{\text{number of osmotically active substances in solution}}{\text{number of molecules in solution}}.$$

Hence, if x be the number of gram-molecules of solute, then the number of osmotically active particles will be $i \times x$, and therefore, the gas law expression for solutions of electrolytes becomes

$$\text{PV} = i x \text{RT}.$$

Whatever may be the true explanation, the van't Hoff factor, i, gives the extent of the divergence of the properties of dilute solutions of electrolytes from those required to satisfy the perfect gas laws.

Arrhenius in 1885 introduced his well-known theory of Electrolytic Dissociation in order to correlate this anomalous behaviour with respect to the gas laws of solutions of electrolytes, with their equivalent conductivities. There was then available, chiefly due to the efforts of Kohlrausch, a considerable number of data regarding the conduction of electricity through solutions. If Ohm's Law be applied to a solution such that the current which can pass through a cube of 1 cm. side from one face perpendicularly to the opposite face and the potential difference between the two faces is 1 volt, then it is found that the current, C ampères, which flows is equal to

$$\frac{1 \text{ volt}}{\text{specific resistance (in ohms)}}.$$

This value is the *Specific Conductivity*, and may be conveniently expressed in terms of $\frac{1}{\text{ohm}}$, or reciprocal ohm, r.o., or sometimes, mho. The *Equivalent Conductivity* is the specific conductivity divided by the number of equivalents of solute dissolved in 1 c.c. of solution. Kohlrausch had in 1876 been able to show by applying Hittorf's Migration Numbers, which refer to the proportion of electricity carried by each type of ion, *viz.*, cation and anion, to the total amount passed through a solution, that the equivalent conductivities of dilute solutions were made up of the sum of the equivalent conductivities, or mobilities, of the

cations and anions into which the electrolyte had dissociated. Knowing from Faraday's Laws of Electrolysis that the quantity of electricity required to liberate from the solution 1 gram-equivalent of ions at each pole is 96,500 coulombs (*i.e.*, 1 Faraday, or 1 F.), and that this is effected, as indicated by Hittorf's work, by the transference of 1 gram-equivalent of ions, cations and anions together, through the solution towards the appropriate electrodes, it is possible to calculate what amount of electricity is carried by each of the two kinds of ions, and therefore to calculate what the conductivity of a solution should be when it contains different amounts of ions. To account for the increase in equivalent conductivity which occurred with the dilution of a solution of an electrolyte, Arrhenius introduced the conception of *Electrolytic Dissociation*, the degree of which was a function of the concentration and which increased with increasing dilution but only became unity when the solution was infinitely dilute. Thus, consider the ionisation which accompanies the dissolution of sodium chloride. In an infinitely dilute solution electrolytic dissociation is considered to take place completely thus :

$$NaCl \rightarrow Na^{\cdot} + Cl'$$

and the equivalent conductivity, Λ_{∞}, to be caused by the conductivities of $Na^{\cdot}$ and Cl' ions, *i.e.*,

$$\Lambda_{\infty} = l_{Na^{\cdot}} + l_{Cl'}.$$

These *ionic conductivities*, l, are often referred to as the *ionic mobilities*.

At any other concentration ionisation is incomplete and of the gram-equivalent of sodium chloride dissolved α gram-equivalent has been converted into ions, which unlike the undissociated molecules of salt, permit the electric current to pass through the solution. Hence we see that the equivalent conductivity, Λ, at any other concentration, is equal to α $(l_{Na^{\cdot}} + l_{Cl'})$, and therefore that the degree of electrolytic dissociation at any particular concentration can be calculated from

$$\alpha = \frac{\Lambda}{\Lambda_{\infty}}.$$
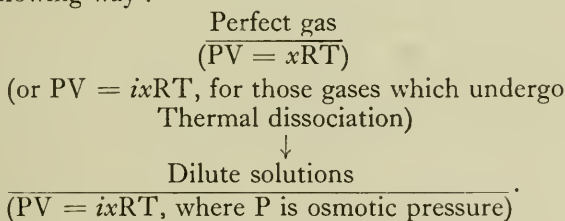
Hence one gram-equivalent of sodium chloride on dissociating produces $(1 - \alpha)$ gram-equivalents of undissociated NaCl molecules and α gram-equivalent each of sodium- and chloride-ions, all of which Arrhenius considered to be capable of exerting osmotic pressure. Instead of having one gram-equivalent of solute molecules, there arises $(1 - \alpha) + \alpha + \alpha = 1 + \alpha$

gram-equivalents of molecules and ions. If this is the true explanation of the variations in equivalent conductivity with dilution, then it is evident that $1 + \alpha$ is equal to van't Hoff's factor referred to above. Arrhenius showed in numerous instances that the degree of electrolytic dissociation as calculated from conductivity data gave figures which compared well with the van't Hoff factor obtained from measurements of either of the thermodynamically related properties of the various solutions, *viz*., osmotic pressure, elevation of boiling-point, lowering of the freezing-point and vapour pressure. Despite the lack of agreement in some few cases, it was considered that the relationship between conductivity and those properties which may be shown to be thermodynamical consequences of the application of the perfect gas laws to dilute solutions had been firmly established. Other fundamental functions which are based on thermodynamical principles involving the validity of the application of the perfect gas laws to solutions are (*a*) that reactions in dilute solutions should obey the Law of Mass Action, (*b*) Nernst's interpretation of the E.M.F. of " concentration cells " and the potential difference which exists between a metal and the solution in which it is immersed. Wilhelm Ostwald applied the Law of Mass Action to the dissociation of weak acids and bases in solutions of varying dilution, and found that the values of the degree of electrolytic dissociation found from conductivity measurements on substitution into the mass law expression gave rise to dissociation or affinity constants which were of uniform magnitude. In these cases the empirical conductivity data and the thermodynamically established mass law were in conformity. This, however, is not so with the strong acids and bases and electrolytes in general. It is, therefore, evident that the state of the modern theory of solutions is far from satisfactory, and for this reason efforts are being made to evolve a more satisfactory one. It is not surprising to find that G. N. Lewis and others disregard conductivity entirely, and consider only those properties which can be shown to be thermodynamically interdependent with the perfect gas laws. In place of ion-concentrations they consider that data are thereby obtained which are a measure of ion-activity. They apply the perfect gas laws to all concentrations, and their data, instead of giving a measure of the extent of ionisation, merely give some idea of the extent of the divergence of the solutions from the gas laws.

It may be pointed out that the perfect gas laws hold in an approximate way for dilute solutions only. They cannot hold for concentrated solutions, for they do not involve such factors, as cohesion and hydration of molecules and ions, whose effect then

become pronounced. Neither do they account for the electro-static forces of attraction and repulsion which most probably exist between the different ions, and which, it would be expected, would be influenced considerably by increase in concentration. This constitutes a fundamental objection to any attempt to apply the theory to all concentrations. In the activity theory, the gas laws are held to be applicable to all solutions and, consequently, the mass law must of necessity hold. Now, it is found that the ion-concentrations of strong electrolytes which can be calculated on the basis of the Arrhenius dissociation theory from conductivity measurements, do not obey the mass law. According to G. N. Lewis this is because the true concentrations (" active masses ") are not employed, and which can only be found from observations of freezing-point, boiling-point, vapour pressure, and the E.M.F's of concentration cells, all of which are thermodynamically inter-dependent with the mass law. Hence, to find these effective concentrations for any particular solution, the actual concentrations have to be multiplied by a factor, the activity coefficient, so found. This factor is important, for the adherents of the activity theory insert it in the Nernst E.M.F. equation, instead of the degree of electrolytic dissociation. These considerations may be summarised in the following way :—

$$\text{Perfect gas}$$
$$(PV = xRT)$$
(or $PV = ixRT$, for those gases which undergo
Thermal dissociation)
$$\downarrow$$
$$\text{Dilute solutions}$$
$$(PV = ixRT, \text{ where P is osmotic pressure})$$

Thermodynamical deductions :—

(a) Mass law to be applicable.
(b) Laws relating to freezing-point, boiling-point, vapour pressures to hold.
(c) E.M.F. expression for " concentration cells."

Electrolytic dissociation (Arrhenius)	Activity (G. N. Lewis)
Non-electrolytes.	Weak electrolytes only.	Weak electrolytes.	Strong electrolytes. (All concentrations.)
(Dilute solutions.)			
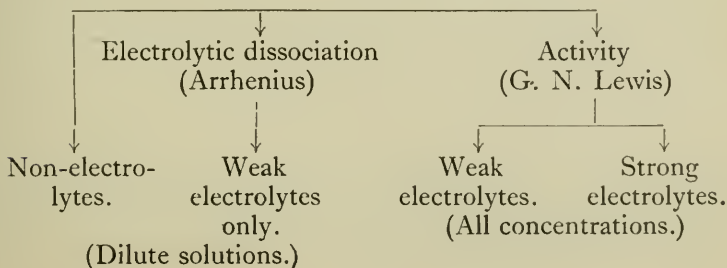
Theory of Electromotive Force Measurements.

As already stated the calculations of ion-concentrations or ion-activities from the potential-differences which are set up between an electrode and a solution are based upon the assumption that the perfect gas laws apply also to dilute solutions. Although such an assumption may not be entirely justifiable, it does provide a basis upon which a fairly plausible explanation of electrode potentials can be obtained. As regards controlling, and if need be, measuring variations in acidity and alkalinity the E.M.F. data of the hydrogen electrode are, indeed, themselves sufficient, without any further effort being made to calculate hydrogen-ion concentrations or pH values. Nevertheless, these calculations yield useful results, and especially is this true when the E.M.F's produced by other electrodes which function in a parallel manner to the hydrogen electrode in the presence of hydrogen- and hydroxyl-ions, and the colour changes of indicators are considered.

We shall now consider the E.M.F. established between a metal and a solution, into which it dips, containing a salt which is ionised giving cations of the metal. Suppose the valency exercised by the metal in forming salts is n, and therefore each gram-ion of the metal carries n positive charges, or in other words is composed of n gram-equivalents which for their deposition from the solution on passing an electric current through it will necessitate a quantity of n Faradays, *i.e.*, $n \times 96,500$ coulombs. We shall assume that at the surface of the metal there exists a tendency for it to dissolve in the solution as atoms, and that some of these atoms are converted into metallic-ions of the same kind as those already present in the solution in the form of a salt. The metal, therefore, may be regarded as possessing an *electrolytic solution pressure* at its interface as postulated by Nernst. There will consequently be established an equilibrium between the cations in solution and the tendency of electrode to produce similar ions. Suppose that x gram-ions are contained in v litres of solution, and that the concentration of the ions is c gram-ions per litre, whence $c = x/v$. Let the volume occupied by x gram-ions liberated from and at the surface of the electrode be V, and the concentration of ions so formed be $C\left(= \dfrac{x}{V} \right)$. The potential difference between the electrode and the solution is E volts, which might be considered as the *Intensity Factor* of the electrical work which would be entailed in driving x gram-ions of metal from the electrode into the solution by the application of the electric current or *vice versa*. The

quantity of electricity required by x gram-ions of n-valent ions will be xnF, where F represents 1 Faraday (96,500 coulombs), and therefore the electrical work to be performed will be equal to xnF $\times$ E (volt)

$$= xn \times 96,500 \times E \text{ volt-coulombs, or joules,}$$
$$= xn \times 96,500 \times E \times 10^7 \text{ ergs.}$$

This work should be carried out in such a way that there is no change in temperature of the solution. This transference of ions might also have been considered as having taken place by virtue of their osmotic pressure, and in this connexion we shall now consider how this might have been done had the ions been in the form of gas molecules. Such an analogy is valid if the perfect gas laws apply equally well to ions in dilute solutions. In Fig. 1 is represented a hollow rectangular prism containing a volume of perfect gas and above which moves a gas-tight, frictionless and weightless cover. To this cover, whose area is a sq. cm., a pressure of P dynes is applied, which thereby causes the cover to move inwards δl cm. This means that a force of P dynes plays upon each square centimetre of the cover, equivalent to a total force of $a \times P$ dynes

Fig. 1.—Isothermal Compression of a Perfect Gas.

acting perpendicularly upon the cover at its centre of gravity. The work done in compressing the gas by the movement of the point of application of this force through δl cm. is

$$a \times P \times \delta l \text{ ergs.}$$

Such work results in the generation of heat by the gas, but if the compression be carried out at a sufficiently slow rate this heat will be radiated to the surroundings without appreciably changing the temperature of the gas. It will be seen that $a \times \delta l$ c.c. is the

decrease in volume of the gas, namely δv, and therefore the work done is equal to

$$P \times \delta v \text{ ergs.}$$

To find the amount of work to be done to compress the gas from volume V litres down to v litres, it is necessary to integrate between the limits $V \times 1{,}000$ c.c. and $v \times 1{,}000$ c.c.   Hence

$$\text{Work} = \int_{v \times 1000}^{V \times 1000} P\,dv, \text{ and as}$$

$$PV = x\text{RT}, i \text{ being unity,}$$

$$\text{Work} = x\text{RT}\int_{v \times 1000}^{V \times 1000} \frac{1}{v} dv$$

$$= x\text{RT} \log_e \frac{V \times 1000}{v \times 1000}$$

$$= x\text{RT} \log_e \frac{V}{v}.$$

$$\text{Also } PV = pv, \text{ and}$$

$$\therefore \text{Work} = x\text{RT} \log_e \frac{p}{P}.$$

Analogously, we see that the work involved in compressing x gram-ions from volume V at the electrode to volume v in the solution is equal to

$$x\text{RT} \log_e \frac{V}{v} = x\text{RT} \log_e \frac{p}{P}.$$

The pressures included in the latter expression are seen to be p the osmotic pressure of the ions in the solution, and P the electrolytic solution pressure of the ions at the metal surface.   We have seen earlier in this chapter that in order to express this osmotic work in terms of the same units, $viz.$, joules, as the electrical work, it is only necessary to put $R = 8\cdot313$ joules per degree Absolute.   Hence, by equating the two expressions giving the amounts of electrical work and osmotic work which are necessary to transfer x gram-ions from metal to solution, we get

$$xn\text{FE (joules)} = x\text{RT} \log_e \frac{V}{v} = x\text{RT} \log_e \frac{c}{C}$$

$$= x\text{RT} \log_e \frac{p}{P} \text{ (joules)},$$

and therefore

$$\text{E volts} = \frac{RT}{nF} \log_e \frac{V}{v} = \frac{RT}{nF} \log_e \frac{c}{C} = \frac{RT}{nF} \log_e \frac{p}{P}.$$

The relation between the E.M.F. of a single metallic electrode and a solution is given by

$$E = \frac{RT}{nF} \log_e \frac{c}{C}$$

$$= -\frac{RT}{nF} \log_e C + \frac{RT}{nF} \log_e c.$$

The expression $-\dfrac{RT}{nF} \log_e C$ includes the hypothetical concentration of metal-ions which have been assumed to exist at the surface of the metal and to have originated from the metal. There is no method available to measure this concentration. It is feasible to assume that each metal has its own particular solubility in water which in the case of those metals that do not react directly with water is extremely small. Of the atoms so dissolved a definite proportion becomes electrically charged in the form of ions and thus determines the E.M.F. of the electrode. When, however, the metal is allowed to dip into a solution already containing those ions, such ions might have some repressing effect on the proportion of ions arising from the electrode surface. Taking for granted that the E.M.F. of a single electrode can be measured when immersed in a solution containing a known concentration of ions, we find that at any given temperature we can calculate what exactly is the concentration C. We also see that when the concentration of ions dissociated from the salt is equal to one gram-ion per litre, *i.e.*, $c = 1$, then the last term becomes zero and thus E then becomes equal to $-\dfrac{RT}{nF} \log_e C$. The value of this term for each particular metal is a constant, and is known as the *Normal Electrode Potential*, or sometimes as the *Electrolytic Potential*. We see from the foregoing that it is the E.M.F. given by any particular metal when immersed in, and in equilibrium with, a solution containing 1 gram-ion of its ions per litre. It varies with temperature as shown by formula. It is usually denoted by either ϵ or " E.P." The expression connecting the E.M.F. with the concentration of ions in the solution may now be written

$$E = \epsilon + \frac{RT}{nF} \log_e c,$$

and further simplified by inserting the values $R = 8.313$, $F = 96,500$, and the factor 2.303 in order to convert the logarithms from the base e to the base 10, whence it is found that

$$E = \epsilon + 0.000,198,4 \frac{T}{n} \log c.$$

At 18° C. ($T = 291°$ A.)

$$E = \epsilon + \frac{0.0577}{n}, \log c$$

and at 25° C. ($T = 298°$ A.)

$$E = \epsilon + \frac{0.0591}{n} \log c.$$

In Table 1 are given the values of $R \times T \times 2.303/F$ for temperatures 15° to 25° C.

TABLE I.

Temp. °C.	15	16	17	18	19	20	21	22	23	24	25
$\frac{RT \times 2.303}{F}$	0·0571	0·0573	0·0575	0·0577	0·0579	0·0581	0·0583	0·0585	0·0587	0·0589	0·0591

In the case of certain non-metals which behave reversibly and therefore may function as electrodes, e.g., iodine, we must take into consideration the direction in which the current flows. With metals which attain equilibrium with positively charged ions viz., cations, the quantity of electricity required to deposit 1 gram-equivalent at the cathode, or to dissolve from the anode, is 1 Faraday, but with non-metals, like iodine which enters into equilibrium with negatively charged ions, anions, we must not forget that on electrolysing, these ions travel against the current, and are either discharged at the electrode at which the current enters the solution or are dissolved from the cathode. The Faraday of electricity associated with 1 gram-equivalent of anions must, therefore, be regarded as negative, and therefore the electrical work involved in driving x gram anions which are n-valent into solution will be equal to $- xnEF$ joules. Hence

$$- xnEF = xRT \log_e \frac{c}{C},$$

and therefore

$$E = + \frac{RT}{nF} \log_e C - \frac{RT}{nF} \log_e c$$

$$= \epsilon - \frac{RT}{nF} \log_e c.$$

Alternate Method of Obtaining Electrode Potential Formulæ using van't Hoff Reaction Isotherm.

In view of the successful application, first by Biilmann, of the quinhydrone electrode for the determination of hydrogen-ion concentrations, we shall now consider how oxidation-reduction equilibria may sometimes be made use of by immersing an electrode of platinum in a solution, where such an equilibrium prevails in order that it might function as a hydrogen electrode and be readily responsive to changes in the concentration of hydrions. Incidentally, we shall see that the above formula can be arrived at in a somewhat different manner. It will be seen from text-books on physical chemistry that not only is the law of mass action a thermodynamic consequence of the application of the perfect gas laws to dilute solutions but so also is the so-called van't Hoff reaction isotherm, which links up the affinity of, or maximum work which can be done by, a reaction if carried out in a manner in which there is no change in temperature of the solution during the process. This is generally true when a reaction is allowed to do electrical work at some given temperature. If we consider the general reaction

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$
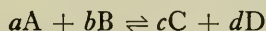
then, by applying the law of mass action we find that

$$\frac{[\mathrm{C}]_\epsilon^c \times [\mathrm{D}]_\epsilon^d}{[\mathrm{A}]_\epsilon^a \times [\mathrm{B}]_\epsilon^b} = \mathrm{K},$$

where the square brackets with suffix ϵ represent the concentrations at equilibrium of the reactants and K, the mass law constant, or affinity constant. The maximum work which the reaction is capable of doing in proceeding from left to right at a given temperature is given by

$$\mathrm{Work} = \mathrm{RT} \log_e \frac{[\mathrm{C}]_\epsilon^c \times [\mathrm{D}]_\epsilon^d}{[\mathrm{A}]^a \times [\mathrm{B}]^b} - \mathrm{RT} \log_e \frac{[\mathrm{C}]^c \times [\mathrm{D}]^d}{[\mathrm{A}]^a \times [\mathrm{B}]^b}$$

$$= \mathrm{RT} \log_e \mathrm{K} - \mathrm{RT} \log_e \frac{[\mathrm{C}]^c \times [\mathrm{D}]^d}{[\mathrm{A}]^a \times [\mathrm{B}]^b}.$$

[C] and [D] represent the respective concentrations of C and D produced by the reaction, and [A] and [B] the respective concentrations of A and B at the beginning. We know that when 1 Faraday of electricity is passed through an electrolyte there is liberated at the cathode 1 gram-equivalent of metal, *i.e.*, 1 gram-equivalent of metal-ions give up their charge and become uncharged

metal. The following equations may therefore be regarded as representing typical reactions taking place at the electrodes :—

$$H^{\cdot} \rightarrow H + 1F \times E_{H^{\cdot}}$$
$$Ag^{\cdot} \rightarrow Ag + 1F \times E_{Ag^{\cdot}}$$
$$Cu^{\cdot} \rightarrow Cu + 1F \times E_{Cu^{\cdot}}$$
$$Cu^{\cdot\cdot} \rightarrow Cu + 2F \times E_{Cu^{\cdot\cdot}}$$
$$Au^{\cdot\cdot\cdot} \rightarrow Au + 3F \times E_{Au^{\cdot\cdot\cdot}}$$
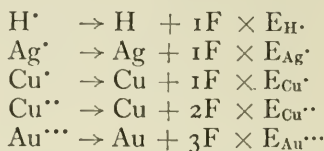
The following reaction is an example of the change which takes place with an anion-forming element :—

$$I \rightarrow I' + 1FE_{I}.$$
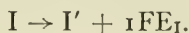
In the above equations the E.M.F's at which these reactions take place are given by E, and thus we see that the products, nFE, give the amount of work necessary to convert one gram-ion of the various cations into the non-ionic state, whereas the reverse is the case of anions. These equations refer to simple processes of reduction, there being decreases in positive valency or otherwise an increase in negative valency. As is well known reduction and oxidation processes may occur entirely between ions. Thus the reducing action of stannous chloride on ferric chloride is shown by the equation

$$2FeCl_3 + SnCl_2 \rightleftharpoons 2FeCl_2 + SnCl_4$$

or, ionically,

$$2Fe^{\cdot\cdot\cdot} + Sn^{\cdot\cdot} \rightleftharpoons 2Fe^{\cdot\cdot} + Sn^{\cdot\cdot\cdot\cdot}.$$
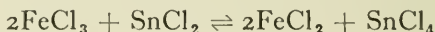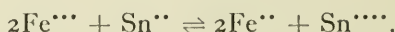
This reaction is seen to be the outcome of two opposing reactions, $viz.$,

$$2Fe^{\cdot\cdot\cdot} \rightarrow 2Fe^{\cdot\cdot} + 2F \times E_{Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}}$$

and

$$Sn^{\cdot\cdot\cdot\cdot} \rightarrow Sn^{\cdot\cdot} + 2F \times E_{Sn^{\cdot\cdot\cdot\cdot} \rightarrow Sn^{\cdot\cdot}}$$
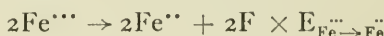
Each of the reduction reactions could have been effected by passing a current at a suitable E.M.F. The amount of electricity required to reduce the valency of a gram-ion by one unit is found to be 1 Faraday, and this accounts for the 2 Faradays shown in the above equations. Organic compounds may often be reduced by means of the electric current, and consequently it is reasonable to assume the quantity of electricity involved is that normally required to discharge the hydrogen-ions as atoms which ultimately enter into combination to form the reduced compound. Quinhydrone is a molecular compound comprising one molecule of

quinone and one of hydroquinone. When dissolved in water an equilibrium is set up between the hydrogen-ions it contains and the constituent compounds, thus :

Quinone (Q)   Anion of
                Hydroquinone (Q'')
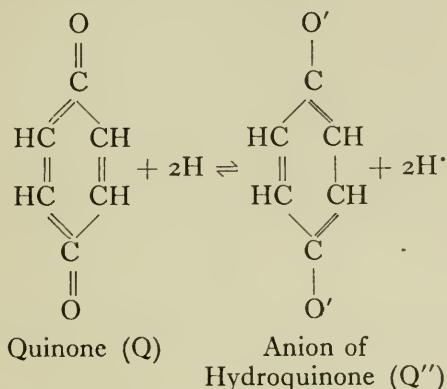
We are now in a position to apply the van't Hoff isotherm to the various reactions, and by equating the maximum work given by this expression to the electrical work involved if the processes had been carried out electrically, we arrive at the formulæ connecting (a) the E.M.F. of simple metallic or non-metal non-metallic electrodes and the respective ion concentrations of the solutions, and (b) the E.M.F. of platinum electrodes, immersed in solution in which equilibria prevail between ions in different stages of oxidation and reduction.

Case I.

Electrodes of the type.—*Metals and Non-metals immersed in Salt Solutions containing their respective ions :*—

(a) Metal-ions of valency n reduced to metal ;
(b) Non-metals reduced to non-metal-ions of valency n.

Reactions :

$$(a)\ \mathrm{M}^{\cdots\cdots n} \to \mathrm{M}\quad + n\mathrm{F} \times \mathrm{E_M}$$
$$(b)\ \mathrm{A}\quad \to \mathrm{A}'''^{\cdots n} + n\mathrm{F} \times \mathrm{E_A}$$
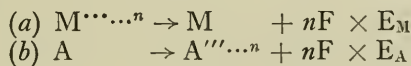
For reaction (a)

$$\mathrm{Work} = n\mathrm{F}\mathrm{E_M} = \mathrm{RT} \log_e \frac{[\mathrm{M}]_\epsilon}{[\mathrm{M}^{\cdots n}]_\epsilon} - \mathrm{RT} \log_e \frac{[\mathrm{M}]}{[\mathrm{M}^{\cdots n}]}.$$

The concentrations denoted by $[\mathrm{M}]_\epsilon$ and $[\mathrm{M}^{\cdots n}]_\epsilon$ are those which were attained when equilibrium was reached ; $[\mathrm{M}]$, the

concentration of metal which was in solution in the atomic state and [$M^{\cdots\cdots n}$], the concentration of metal-ions. Now the concentrations of atomic metal in solution, [M]$_e$ and [M], are due to the solubility of the metal in the salt solution, which in all probability is scarcely affected by different concentrations of its ions that may be in the salt solution in which the metal is placed. Hence [M]$_e$ = [M] and therefore

$$\text{Work} = n\text{FE}_M = -\text{RT}\log_e [M^{\cdots n}]\epsilon + \text{RT}\log_e [M^{\cdots n}]$$

and

$$\text{E}_M = -\frac{\text{RT}}{n\text{F}}\log_e [M^{\cdots n}]\epsilon + \frac{\text{RT}}{n\text{F}}\log_e [M^{\cdots n}]$$

$$= \epsilon_M + \frac{\text{RT}}{n\text{F}}\log_e [M^{\cdots\cdots n}].$$

Similarly for a non-metallic electrode A in equilibrium with ions $A^{\prime\prime\prime\cdots n}$; reaction (b),

$$\text{E}_A = \epsilon_A - \frac{\text{RT}}{n\text{F}}\log_e [A^{\prime\prime\prime\cdots n}].$$

It will be observed that these expressions are identical with those obtained in the preceding paragraph, and the characteristic constants, ϵ_M and ϵ_A, have the same significance being the normal electrode or electrolytic potentials.

Case II. (a)

Electrodes of the type.—*Platinum dipping in a solution containing ions of the same element but with different valencies.*
Reactions :

(a) Cations $M^{\cdots m}$ (*m* positive charges) and
$M^{\cdots n}$ (*n* positive charges), *m*
being *greater* than *n*
$M^{\cdots\cdots m} \rightarrow M^{\cdots\cdots n} + (m - n)\text{FE}_M$

(b) Anions $A^{\prime\prime\prime\cdots m}$ (*m* negative charges) and
$A^{\prime\prime\prime\cdots n}$ (*n* negative charges), *m*
being *less* than *n*.
$A^{\prime\prime\prime\cdots m} \rightarrow A^{\prime\prime\prime\cdots n} + (n - m)\text{FE}_A.$
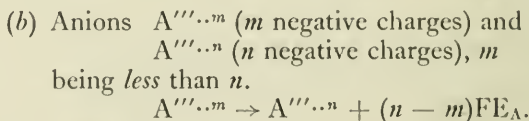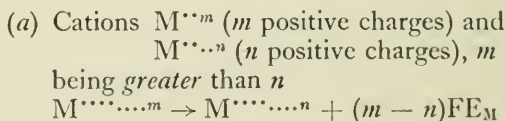
Each of the processes (a) and (b) represent reductions, with, in the first reaction, a *diminution* in positive valency, (= (m − n) equivalents), and in the second, an increase in negative valency (= (n − m) equivalents). Examples of the first class are ferric-ferrous, and stannic-stannous ions equilibria, and of the second

equilibria involving ferricyanide and ferrocyanide ions. For reduction of *cations* (a)

$$\text{Work} = (m - n)\text{FE} = \text{RT} \log_e \frac{[\text{M}^{\cdots n}]_\epsilon}{[\text{M}^{\cdots m}]_\epsilon} - \text{RT} \log_e \frac{[\text{M}^{\cdots n}]}{[\text{M}^{\cdots m}]},$$

whence

$$\text{E}_{\text{Cations}} = \frac{\text{RT}}{(m - n)\text{F}} \log_e \frac{[\text{M}^{\cdots n}]_\epsilon}{[\text{M}^{\cdots m}]_\epsilon} - \frac{\text{RT}}{(m - n)} \log_e \frac{[\text{M}^{\cdots n}]}{[\text{M}^{\cdots m}]},$$

and for *anions* (b)

$$\text{Work} = (n - m)\text{FE} = \text{RT} \log_e \frac{[\text{A}''^{\cdots n}]_\epsilon}{[\text{A}''^{\cdots m}]_\epsilon} - \text{RT} \log_e \frac{[\text{A}''^{\cdots n}]}{[\text{A}''^{\cdots m}]}.$$

$$\text{E}_{\text{Anions}} = \frac{\text{RT}}{(n - m)\text{F}} \log_e \frac{[\text{A}''^{\cdots n}]_\epsilon}{[\text{A}''^{\cdots m}]} - \frac{\text{RT}}{(n - m)\text{F}} \log_e \frac{[\text{A}''^{\cdots n}]}{[\text{A}''^{\cdots m}]}.$$

Both the above expressions involve a term corresponding to concentrations of the ions when in a state of equilibrium. These terms are of constant value and are characteristic of the particular reduction processes which may be considered. If reactions be considered for which there are available equal concentrations (a) of $[\text{M}^{\cdots n}]$ and $[\text{M}^{\cdots m}]$ and (b) of $[\text{A}''^{\cdots n}]$ and $[\text{A}''^{\cdots m}]$ then the last terms in the respective formulæ become equal to zero and therefore the E.M.F. between the platinum electrode and the solution becomes equal to the first term in each case. Thus, it is seen that the first term corresponds to the E.M.F. set up when the reductions have proceeded half-way. Such E.M.F's are constant at a given temperature for a given reaction, and are known as the *Normal Reduction Potentials*. Naturally they constitute a valuable index of the power of the oxidising or reducing action of any particular reagent. These equations may therefore be re-written

$$\text{E} = \epsilon_{\text{oxidised ions} \rightarrow \text{reduced ions}} - \frac{\text{RT}}{n\text{F}} \log_e \frac{[\text{reduced ions}]}{[\text{oxidised ions}]}.$$

One of the chief difficulties encountered in using the hydrogen electrode is the readiness with which the hydrogen in presence of platinum black may be utilised in reducing any reducible substances that may be present in the solution. It is probable that in this case the hydrogen is present in the atomic state, for its behaviour then appears to be comparable with that of so-called nascent hydrogen. If the solution contains ferric ions, for example, reduction ensues immediately and the electrodes are rendered useless. The withdrawal of the atomic hydrogen from a hydrogen electrode may be represented thus :

$$\text{Fe}^{\cdots} + \text{H} \rightleftharpoons \text{Fe}^{\cdot\cdot} + \text{H}^{\cdot}.$$

2
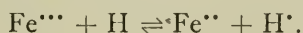
Applying the van't Hoff isotherm to the reaction having the higher normal reduction potential, we find that the potential assumed by the hydrogen electrode when all its hydrogen has been utilised in the catalytic reduction of the $Fe^{...}$ ions will be governed by the ratio of the concentrations of ferric- to ferrous-ions. The electrode will consequently function as a platinum electrode, whose potential

$$E = \frac{RT}{F} \log_e \frac{[Fe^{..}]\epsilon}{[Fe^{...}]\epsilon} - \frac{RT}{F} \log_e \frac{[Fe^{..}]}{[Fe^{...}]}.$$

Thus the potential of a hydrogen electrode in a solution in which it is effecting reduction of ions of the nature of ferric will not be influenced by the concentration of hydrogen-ions in the solution.

We shall now discuss the equilibrium between quinone and hydroquinone in which, due to the slight solubility of quin-hydrone, the ratio of oxidised to reduced portions is kept equal to unity, and as a result the variation in the potential difference between a platinum electrode and a solution containing quin-hydrone is over a certain range purely a function of hydrogen-ion concentrations.

Case II. (b).

Type of Electrode.—Platinum electrode dipping into solution containing quinhydrone.

Of the two constituent reactions given on page 15 the one having the higher Normal Reduction Potential is

Quinone (Q) $\rightleftharpoons$ Anion of Hydroquinone (Q'') + $2FE_Q$.

Hence the potential of a platinum electrode immersed in a solution in which an equilibrium prevails between Q and Q''-ions, will be given by

$$E_{Quin.} = \frac{RT}{2F} \log_e \frac{[Q'']\epsilon}{[Q]\epsilon} - \frac{RT}{2F} \log_e \frac{[Q'']}{[Q]}.$$

Thus the reduction potential of quinone is determined directly by the ratio of the dibasic anions of hydroquinone to the quinone present. This concentration of anions is, however, dependent not only upon the total concentration of hydroquinone, *i.e.*, in the undissociated and ionised condition, but upon the hydrogen-ion concentration of the solution. As each of the hydroxyl groups of hydroquinone, H_2Q, are capable of ionisation, which we may represent thus,

$$H_2Q \rightleftharpoons H^{\cdot} + HQ'$$

for which
$$K_1 = \frac{[H^{\cdot}][HQ']}{[H_2Q]},$$

and
$$HQ' \rightleftharpoons H^{\cdot} + Q''$$
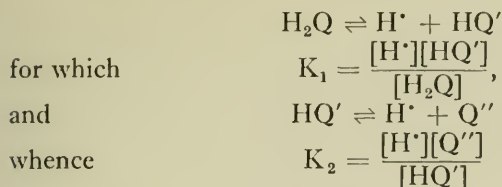
whence
$$K_2 = \frac{[H^{\cdot}][Q'']}{[HQ']}$$

we see that the *total concentration of hydroquinone*, [hydroquinone],

$$= [H_2Q]_{(undissociated)} + [HQ'] + [Q'']$$
$$= \frac{[H^{\cdot}][Q'']}{K_1 \cdot K_2} + \frac{[H^{\cdot}][Q'']}{K_2} + [Q''].$$

Hence

$$[Q''] = \frac{K_1 \cdot K_2}{[H^{\cdot}]^2 + K_1[H^{\cdot}] + K_1 \cdot K_2} \times [hydroquinone],$$

and therefore

$$E_{Quin.} = \epsilon_Q - \frac{RT}{2F} \log_e \frac{[hydroquinone]}{[quinone]} \times \frac{K_1 \cdot K_2}{[H^{\cdot}]^2 + K_1[H^{\cdot}] + K_1K_2}$$

i.e.,

$$E_{Quin.} = \epsilon_Q + \frac{RT}{2F} \log_e K_1K_2 + \frac{RT}{2F} \log_e \frac{[quinone]}{[hydroquinone]}$$
$$+ \frac{RT}{2F} \log_e \left([H^{\cdot}]^2 + K_1[H^{\cdot}] + K_1K_2\right).$$

The first two terms are constants and the third term becomes equal to zero in the case of quinhydrone, for the quinone and hydro-quinone are present in an equimolecular ratio. K_1 and K_2 are of the order of 10^{-10} and 10^{-12} respectively and therefore in a solution whose *p*H is smaller than 8, $K_1[H^{\cdot}]$ and $K_1 \cdot K_2$ are of negligible magnitude.

Consequently

$$E_{Quin.} = a \text{ constant } (\lambda) + \frac{RT}{2F} \log_e [H^{\cdot}]^2,$$

i.e.,
$$E_{Quin.} = \lambda + \frac{RT}{F} \log_e [H^{\cdot}].$$

The value of λ can be determined by comparison with the hydro-gen electrode, thus giving to a platinum electrode an E.M.F. which varies with the hydrogen-ions present and whose concen-trations can be calculated.

Single Electrode Potentials.

Hitherto we have tacitly assumed that the potential differences between individual electrodes and any solutions in which they may be immersed could be measured. This, however, is not the case. We can only measure the potential difference between two electrodes dipping in the same solution, or else, in different solutions which are connected with one another by means of a suitable junction. There is also a distinct possibility of potential differences being established at the points of contact of the different solutions present in the cell. There is very good evidence for the belief that these can be eliminated almost entirely by inserting a saturated solution of potassium chloride between the two electrode solutions. If it were only possible to know the potential difference between one particular electrode and a solution, then cells could be made up involving this electrode, or as it is sometimes called half-element, and an unknown electrode, and from the observed voltage, the E.M.F. of the unknown electrode could readily be found. Thus if a cell were composed such that the more positive electrode was at a potential of E_1 volts and the other electrode at E_2 volts, then the E.M.F. which could be measured between the two electrodes would be equal to $E_1 - E_2$ volts ; *i.e.*, the observed E.M.F. of cell

$$= E_1 - E_2 \text{ volts.}$$

Until the absolute potential of such a half-element can be determined, it has been found convenient to assign to one particular electrode system an arbitrary potential, thus rendering it possible to calculate the relative potential differences of any other electrodes and solutions, and to compare the electromotive behaviour of the different electrodes. The usual convention is equivalent to saying that the normal electrode potential of hydrogen is zero. Hence the equation connecting the E.M.F. of a hydrogen electrode and the concentration of hydrogen ions of the solution becomes at $18°$ to $20°$ C.

$$E = o + o \cdot o58 \log [H^{\cdot}].$$

Electrode of Arbitrary Zero Potential.

Though at different times no less than three electrodes have been taken as being of zero potential, the so-called *Normal Hydrogen Electrode* is now generally assumed to be of zero potential. This arbitrary zero electrode is the ordinary hydrogen electrode in equilibrium with hydrogen gas at one atmosphere pressure, *i.e.*,

760 mm. of hydrogen alone, and a hypothetical solution contain-
ing 1 gram-molecule of hydrogen-ions per litre. This electrode,
furthermore, is usually assumed to be of zero potential for all
temperatures. At the time this convention was made there was
only one way by which hydrogen-ion concentrations could be
calculated, namely, from conductivity measurements, and con-
sequently it was not a difficult matter to prepare a solution whose
hydrogen-ion concentration could be regarded as *one*-Molar, as
required by the normal hydrogen electrode. Nowadays, some
little confusion has arisen through the introduction by G. N.
Lewis of the activity theory, and, therefore, instead of using the
degree of dissociation for the purpose of calculation, the exponents
of that theory employ the hypothetical " activity-coefficient."
We shall in this book assume the correctness of conductivity
data as leading to the true concentration of hydrogen-ions. Though
this view may be unjustifiable, it seems both more convenient and
satisfactory.

CHAPTER II.

Calomel Electrodes.

ALTHOUGH the normal hydrogen electrode provides a very convenient arbitrary zero of potential, it is by no means a suitable practical standard. Perhaps the most suitable standard half-elements are those of potassium chloride solutions of definite concentration which are saturated with pure mercurous chloride, calomel, and which have attained equilibrium with mercury. The concentrations of potassium chloride solution which are used are 0·1N, 1·0N, 3·5N and saturated, and the resulting electrodes are respectively known as decinormal, normal, 3·5 normal and saturated calomel electrodes. The origin of the potential differences which are set up between the mercury and the various solutions lies in the fact that the mercurous chloride is sufficiently soluble to furnish the solution with mercurous-ions. Hence we see from Chapter I that the E.M.F. thus established is given by

$$E = \epsilon_{Hg^{\cdot} \to Hg} + 0·058 \log [Hg^{\cdot}]$$

at 18° to 20° C. The common ion, *viz.*, chloride, in the potassium chloride solution depresses the solubility of the calomel, with the result that with increasing concentrations of potassium chloride the mercurous-ion concentration becomes diminished and so reduces the value, E, the electrode potential. This will be understood from a consideration of the solubility product of the calomel, $L = [Hg^{\cdot}] \times [Cl']$, for when $[Cl']$ is made large by virtue of a greater concentration of potassium chloride, $[Hg^{\cdot}]$ must become correspondingly lower to maintain the constancy of the solubility product, L. These half-elements, once set up, give rise to stable P.D's and which are only slightly affected by temperature. Their precise potentials are ascertained by measuring the fall in potential between a calomel electrode and a hydrogen electrode immersed in a solution of known hydrogen-ion concentration when connected together by means of a saturated solution of potassium chloride. It is, of course, unnecessary to prepare the particular hydrogen electrode which is assumed to have zero

potential, for it is an easy matter to calculate from the observed E.M.F. the exact potential difference which would have been created had it been used. In a cell composed of these electrodes the calomel electrode would be the positive electrode and the hydrogen the negative. If E_{cal} represents the potential of the calomel electrode and E_{H_2} the potential of the hydrogen electrode used, then the observed E.M.F., which drives the current from the calomel to the hydrogen electrode through the wire which joins them, is equal to

$$E_{cal} - E_{H_2} \text{ volts, and as}$$
$$E_{H_2} = 0.058 \log [H^{\cdot}] \text{ at } 18° \text{ to } 20° \text{ C,}$$

of which $[H^{\cdot}]$ is known, we can calculate the value of E_{H_2} and so find the extent by which this hydrogen electrode differs from that of the normal hydrogen electrode. As a rule the hydrion concentration will be less than 1-Molar, and therefore the E.M.F. due to the hydrogen electrode will be more negative than the normal hydrogen electrode. Thus, when the concentration of hydrogen-ions is decimolar, then the expression $0.058 \log [H^{\cdot}]$ becomes equal to $- 0.058$ volt with respect to the arbitrary zero ; when $[H^{\cdot}]$ is equal to 10^{-2} gram-ions per litre $E_{H_2} = - 0.116$ volt, and so on. If we take x as being the actual number of volts by which the potential of the hydrogen electrode employed differs from the arbitrary zero electrode, then we see that if the concentration of hydrogen-ions be greater than 1-Molar x is positive, and becomes negative if less than 1-Molar. Hence in the first instance, the observed

$$\text{E.M.F.} = E_{cal} - E_{H_2},$$
$$= E_{cal} - x \text{ volt,}$$

and in the second case, the observed

$$\text{E.M.F.} = E_{cal} - (- x)$$
$$= E_{cal} + x \text{ volt.}$$

In this way we obtain the P.D. of the calomel half-element re-ferred to the normal hydrogen electrode. That the potential of the calomel electrode merely gives the voltage it is above the arbitrary zero will be evident from Fig. 2.

The " Potential Commission " of the Bunsen Gesellschaft decided in 1911 that the most satisfactory value of the potential of the normal calomel electrode was $+ 0.283$ volt, and $+ 0.337$ volt for the decinormal calomel electrode. Of these, the latter suffers very little change in voltage with temperature, so much so

that Auerbach suggested that it could safely be taken as 0·3370 volt between 20° and 30° C. Discrepancies of two or three milli-volts arise from the ionisation of the various hydrochloric acid solutions which have been used in the hydrogen electrodes against which the calomel electrodes have been compared. Every care must be taken when using either of these two standard elec-trodes to protect them from any variation in the concentration of their potassium chloride, and this is especially apt to occur through possible diffusion of the saturated potassium chloride solution em-ployed as junction liquid. To obviate such alterations Michaelis introduced the saturated calomel electrode. The great drawback to this electrode as a standard lies in the fact that the influence which temperature has on the solubility of potassium chloride causes it to undergo greater changes in P.D. than either the normal

Case I
$[H^{\cdot}] > 1$ Molar

Case II
$[H^{\cdot}] < 1$ Molar
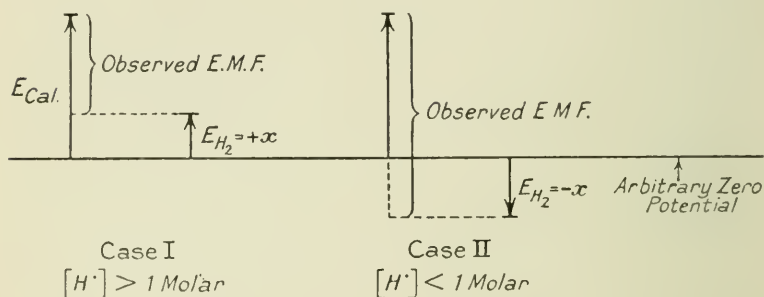
FIG. 2.

or tenth normal electrodes. It is therefore necessary when using it to standardise it against the more constant decinormal calomel electrode. According to Michaelis it varies from + 0·2525 volt at 15° down to + 0·2458 volt at 25° C., whereas the variation in the decinormal calomel is from + 0·3377 to 0·3364 volt for tempera-tures ranging from 18° to 30° C. The potential of the saturated electrode at 18° is + 0·2503 volt; at 19° + 0·2495, and at 20° C. + 0·2488 volt. Sørensen and Linderstrøm-Lang (*Comp. rend. Lab. Carlsberg*, 1924, **15**) assign the following values to the various calomel electrodes at different temperatures :—

Decinormal calomel + 0·3380 + 0·00006 $(t - 18°)$
Normal calomel   + 0·2864 + 0·00024 $(t - 18°)$
3·5 Normal calomel + 0·2549 + 0·00039 $(t - 18°)$
Saturated calomel   + 0·2504 + 0·00065 $(t - 18°)$.

It should be borne in mind that the E.M.F's as calculated from these expressions refer to that of the normal hydrogen electrode, as previously defined, at the appropriate temperature. Actually, however, the normal hydrogen electrode becomes more negative with increasing temperature by 0·00085 volt per degree, and therefore if this had to be taken into consideration we should find that the temperature coefficients of the calomel electrodes would have been very different, *e.g.*, 0·00085 − 0·00006 = 0·00079 volt per degree for N/10 calomel and 0·00085 − 0·00065 = 0·00020 for the saturated calomel electrodes.

Preparation of Calomel Electrodes.

In making calomel electrodes every care must be taken to use pure materials and also to be certain that the solid phase, the calomel, has entered into complete equilibrium with the potassium chloride solution. It must be saturated with calomel, and in this regard an electrode should not be used until it has acquired a steady and correct potential. It is well known that the initial solubility of a difficultly soluble substance is in some way connected with the fineness of its particles, and also with its condition, whether it has just been precipitated and not allowed to dry or else has been prepared for some time and dried. Thus Hulett (*Z. physikal. Chem.*, 1901, **37**, 384) has found that the solubility of barium sulphate when in the form of fine particles of average diameter of 0·00004 cm. is almost twice that of coarser particles whose average diameter is 0·00018 cm. The fact that the smaller particles dissolve more rapidly and also appear to have a higher solubility, no doubt due to a false equilibrium being created, can be traced to the relatively much greater total surface which they have compared with their mass, with the result that a greater solvent action can take place through the increased interfacial tension effects which come into play. As the effect of the surface tension of liquid is to make the exposed surface smaller, *e.g.*, the surface in contact with that of a particle, we see why such forces when acting upon the surface of a particle will tend to cause the particle to dissolve, and furthermore, why those particles which are allowed to separate from a supersaturated solution under conditions which permit surface tension to become effective, result in larger grains. Once a substance, especially a sparingly soluble one, has formed a slightly supersaturated solution, thereby corresponding to a state of false equilibrium, it is often a difficult matter to destroy such a state of affairs. Hence the importance of precipitating the calomel very slowly, by adding the hydrochloric acid drop by drop

and stirring well. It is probable that the best conditions for preparing calomel for electrodes are obtained in the electrolytic preparation.

There is no doubt that ageing tends to reduce the rate at which dissolution can proceed, while on the other hand a freshly formed precipitate when placed in an aqueous solution readily attains equilibrium with it, and may even supersaturate the solution. Such factors would have their effect on the E.M.F. of a calomel electrode on account of the changes in mercurous-ion concentration. The necessity of using pure materials will be understood when it is remembered that mercury may often contain base metals, and calomel may contain traces of soluble mercuric chloride which, if not eliminated, would create an equilibrium between the mercury and the mercuric-ions so introduced into the electrode.

Unless pure mercury is available it will be necessary to subject the commercial product to a treatment with nitric acid of density 1·1 to 1·2 by allowing it to drop down through a column of the acid for about six hours in order to remove any soluble material, then to oxidise any zinc remaining in the mercury by means of air, or by shaking with a dilute solution of potassium permanganate, and finally distil in *vacuo* at low temperature. The last process may often safely be omitted, when the zinc and lead oxides which will rise to the surface have been removed, and the remaining mercury dropped through a length of nitric acid and then forced through a U-capillary tube, 1 mm. in bore, when it will emerge dry.

Calomel of the purity demanded by the British Pharmacopœia is satisfactory, but in case it is desired to prepare it, the following note is given. Some pure mercury is partly dissolved in pure diluted nitric acid, and then hydrochloric acid (s.g. 1·1) is added drop by drop to the solution, in which free mercury is present, with thorough shaking. Decant the clear liquid from the precipitated calomel, wash the calomel-mercury mixture thoroughly with several changes of water and finally a few times with potassium chloride solution of the concentration to be employed subsequently in the electrode. It may also be prepared by electrolysing a normal solution of hydrochloric acid between a platinum cathode and pure mercury, kept well stirred by paddles, as anode (*vide* Lipscomb and Hulett, *J. Amer. Chem. Soc.*, 1916, **38**, 21, and Ewing, *ibid.*, 1925, **47**, 301). A 4-volt accumulator should be used. The calomel so obtained is of a more uniform grain and is mixed with mercury. Before use it must be washed with water and repeatedly with the potassium chloride solution. Unless potassium chloride of A.R. quality can be obtained, the commercial product should be purified by recrystallisation.

Various forms of vessel are used for calomel electrodes, though as far as accuracy and efficiency are concerned it is immaterial which shape is actually chosen. The author generally uses the simple form represented in Fig. 22, which is a wide-necked, two to four ounce bottle and tightly fitted with a rubber bung through which three glass tubes are passed. Into the closed end of the middle one, which *dips below the level of the mercury layer*, is sealed a piece of platinum wire in order to make contact with the mercury. External contact with the platinum wire is made by placing a little mercury in the tube in which is inserted a copper wire having its end amalgamated. The copper lead may, of course, be brought into direct contact with the platinum wire by soldering the two wires together before sealing the platinum into the tube. Above the mercury which is sufficient to cover completely the protruding end of the platinum wire, a paste of calomel and mercury is placed, and above this is the solution of potassium chloride of the desired concentration, either o·1 M, 1·0 M, 3·5 M, or saturated, which must be saturated with calomel. The tube bent at an obtuse angle is fitted tightly with a rubber bung. Its lower end is not allowed to dip into the solution. The tube is used to blow solution into, or out of, the connecting tube which dips into the liquid. After the connecting tube, whose outer end is tapered off some-what, has been dipping into the saturated potassium chloride solution in the junction vessel there is every possibility that the solution in the tube may thereby have become contaminated, and this is guarded against by flushing out the tube with fresh liquid from the electrode vessel after each experiment. Needless to say, all bungs and tubes should fit perfectly in order to make the vessel air-tight, so that no solution actually leaves the connecting tube during determinations. Some little interchange of solution is inevitable at the point where the tube dips into the junction liquid, but any evil effects which might produce an alteration in the con-centration of the solution in the electrode vessel can be avoided by taking these precautions. Although much has been written as to the possible effects which the manner of preparing the mer-cury-calomel paste may have on the potential of the particular electrode, it is probable that appreciable differences will not be caused if the paste is composed of an intimate mixture of finely divided mercury and calomel particles. Errors are only likely to be introduced by the presence of coarse calomel particles, on account of the sluggishness with which they attain equilibrium with the solution, and the poorness of contact with the mercury which may result. The paste may be made by grinding, but not excessively, calomel with mercury in a mortar using a little of the

potassium chloride solution ; after washing several times by decantation the paste is thoroughly shaken with more potassium chloride solution and then poured into the electrode vessel. Some workers advocate merely shaking the calomel with mercury in the potassium chloride solution without resorting to grinding. There is probably no great efficacy in either method—the great point is to ensure as far as possible that true equilibrium is reached between the solid and liquid phases. Other forms of calomel electrode vessels are given in Fig. 3. Their special advantage lies in the fact that being small they necessitate the use of less of the components ; in the first type contact is made with the mercury through a platinum wire which is sealed into the bottom of the vessel, and in the second form by means of a tube, containing
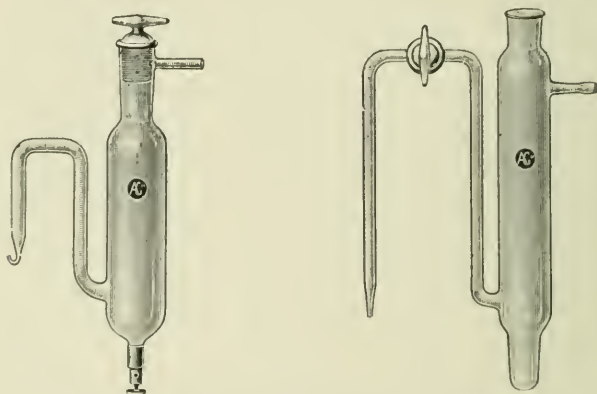
FIG. 3.—Forms of Calomel Electrode Vessels.

mercury and a platinum wire sealed into its closed end, which passes through a rubber bung fitting tightly into the mouth of the vessel. The tap in the connecting arm is an advantage in that it can be employed to reduce the size of the orifice, and so tend to make diffusion more difficult. Closing the tap while the electrode is not being used prevents evaporation of the electrode solution, though in the case of saturated potassium chloride solution this is immaterial. The side tubes shown in both forms are closed with rubber tubing and clips. Yet another modification is to be seen in Fig. 31, in which a tap is inserted in the connecting tube and also a funnel into which saturated potassium chloride solution is placed which may be run into the outer portion of the arm and so serve as junction liquid. Although very convenient for electrometric titration great care must be taken, if accurate E.M.F's are also aimed at, to prevent any possible leaking into the electrode.

Such a form is very suitable when using the saturated potassium chloride-calomel electrode.

The voltages of half-elements, including some that are occasionally used as being of known potential, are given in the following table, which were taken from Ostwald-Luther-Drucker, *Physiko-Chemische Messungen*, 4th Edition, 1925 :—

TABLE 2.

POTENTIALS (VOLTS) OF HALF-ELEMENTS.

Electrode.	ϵ_h at 18° C.	ϵ_h at 25° C.
H_2 | $N - H^{\cdot}$	0·000	0·000
Hg | $HgCl$. 0·1 N — KCl	+ 0·336	+ 0·336
Hg | $HgCl$. 1·0 N — KCl	+ 0·284	+ 0·283
Hg | $HgCl$. 3·5 N — KCl	+ 0·252	+ 0·250
Hg | $HgCl$. 0·1 N — HCl	+ 0·335	+ 0·335
Ag | $AgCl$. 0·1 N — KCl	+ 0·292	+ 0·290
Ag | $AgCl$. 0·1 N — HCl	+ 0 291	+ 0·289
H_2 | 0·1 N — HCl	— 0·063	— 0·064
H_2 | 0·1 N — H_2SO_4	—	— 0·073
Hg | Hg_2SO_4 . 0·1 N — H_2SO_4	—	+ 0·682
H_2 | 0·1 N — NaOH	— 0·759	— 0·761
Hg | HgO . 0· 1 N — NaOH	—	+ 0·165

Other forms of electrode vessel have been described with a view to minimising the risk of diffusion, sometimes by attentuating the connecting arm and sometimes by introducing several U-bends. To guard against possible diffusion the author keeps the level in the electrode vessel slightly higher than that in the vessel containing the saturated potassium chloride. This tends to cause the liquid to flow out of the electrode tube and so militates against any diffusion taking place. For further information regarding the reproducibility of calomel electrodes the reader is referred to Veibel (*J. Chem. Soc.*, 1923, **123,** 2206).

Standard Quinhydrone Electrode.

Veibel (*loc. cit.*) has shown that an electrode comprising a piece of bright platinum foil immersed in a solution containing quinhydrone and 0·01 normal with respect to hydrochloric acid and 0·09 normal with respect to potassium chloride has, at 18° C.,

an E.M.F. of $+$ 0·7040 $\pm$ 0·0002 volt above the hydrogen elec-
trode in equilibrium *with the same electrolyte*, and 0·2485 $\pm$ 0·0002
volt above the potential of the decinormal calomel electrode.   It
is readily reproduced and is durable for at least two days.   As the
0·1 N-calomel electrode is more positive than the normal hydrogen
electrode by $+$ 0·337 volt, we find that the E.M.F. of this special
quinhydrone electrode is $+$ 0·586 volt when referred to the ar-
bitrary zero potential.   It can conveniently be set up in a calomel
electrode vessel of the form shown in Fig. 3 (*b*), fitted with a
rubber stopper through which is passed a tube containing mercury
in contact with a platinum wire sealed into the bottom end, and to
the other end of the wire is fused a strip of bright platinum foil.

Donnan-Allmand Standard Electrode.

An electrode which is sometimes used is one in which mercury
is placed in either N- or $N/_{10}$-solution of sodium hydroxide
or a N-potassium hydroxide solution kept saturated with mer-
curic oxide by means of an excess of fairly coarse-grained mercuric
oxide.   This oxide may be prepared by heating either mercuric
or mercurous nitrate gently in a porcelain basin, with constant
stirring and occasional cooling and gentle grinding until all the
oxides of nitrogen have been driven off.   These products, which
are light reddish-brown, contain very little of the extremely small
particles, and consequently permit of the rapid attainment of
equilibrium as shown by the constancy of the E.M.F.   Donnan
and Allmand (*J. Chem. Soc.*, 1911, **99,** 845) found that if the cor-
rectness of the *Planck liquid potential formula* be assumed, these
electrodes are more positive than the normal hydrogen electrode
as shown by the following expressions :—

E.M.F. of Hg | HgO . N $-$ KOH $= +$ 0·1100 $-$ 0·00011 $(t - 25°)$
E.M.F. of Hg | HgO . N $-$ NaOH $= +$ 0·1135 $-$ 0·00011 $(t - 25°)$
E.M.F. of Hg | HgO . N/10 $-$ NaOH $= +$ 0·1690 $+$ 0·00007 $(t - 25°)$

(These values are based on the potential of the N-calomel
electrode being $+$ 0·283 volt at 18°.)

CHAPTER III.

THE HYDROGEN ELECTRODE AND pH.

In order to make a hydrogen electrode advantage is taken of the large absorptive powers for hydrogen of finely-divided platinum, and sometimes of either palladium or iridium when electrolytically deposited on the bright surfaces of one of these metals, though gold is sometimes used, and of the tendency possessed by these metals to promote catalytically the change, from the molecular condition of hydrogen to the atomic and thence to the ionic state. Care must be taken to prepare electrodes in which this catalytic behaviour is not too great, otherwise they will respond to the slightest disturbing condition, such as traces of reducible substances, even though they may only be reduced with difficulty, instead of establishing rapidly equilibrium with the hydrogen-ions in the solution. In practice, it is often more convenient to use the hydrogen electrode in solutions exposed to the air. This will necessitate the use of electrodes which are either indifferent to possible traces of dissolved oxygen or else will rapidly reduce them and almost immediately attain equilibrium with the hydrions. The simplest form of electrode is that described by Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847). It comprises a rectangular piece of platinised platinum foil connected by a platinum wire to a glass tube containing mercury. This tube is enclosed in another tube having an inlet for hydrogen and a bulb to surround the platinum foil. This bulb is perforated usually at the bottom and in front of the foil and behind, such that when the electrode is immersed in solution and the hydrogen is passing, the foil is about half immersed (Fig. 22). The commercial hydrogen now supplied under pressure in cylinders is usually sufficiently pure for routine work, without any further purification, and by the careful adjustment of its flow can be employed for the dual purpose of maintaining the platinum black in a saturated condition and also in keeping the solution, being tested, thoroughly mixed.

The chief processes worked industrially for the manufacture of hydrogen are by electrolysis and by separation from "water gas". The only impurities likely to be encountered in electrolytically prepared hydrogen are traces of air and carbon dioxide which

may be removed by passing the gas through bubblers containing
alkaline pyrogallol and potassium hydroxide solutions respec-
tively. Moser (Z. anorg. Chem., 1920, **110,** 125) states that iron
carbonyl can often be detected in hydrogen prepared from " water
gas," but if it is present in the hydrogen manufactured in this
country the amount is so minute that it is without any dele-
terious effects on the hydrogen electrode.

If a hydrogen electrode is to be used in a solution containing
no reducible substances, then it does not very much matter what
form the platinum electrode takes, whether it be foil or whether
it be wire, or how the absorptive covering has been deposited,
which may be either of platinum, palladium or iridium black. The
speed with which the electrode attains to a state of equilibrium
with the solution will depend upon the nature of the deposit. Too
heavy a deposit will make the electrode very sluggish, though it
must be conceded that such an electrode will tend to, and will,
attain equilibrium if allowed sufficient time. When reducible
substances are present the author found that the hydrogen soon
became removed from the coating on wire electrodes, whereas
when larger electrodes were used, and provided they were covered
with the right kind of black, they sometimes did not respond to
such influences.

Though it is undoubtedly upon the nature of the " black "
coating that the efficiency of the electrode depends, the author, in
common with many other workers, has failed to determine just
those conditions which lead to the best deposition. It is in some
way connected in the first place with the quality of the surface,
platinum or gold, upon which the black layer is deposited. Those
surfaces should be as highly polished as possible—this was often
done by removing the old platinum black layer with the finest
moistened emery powder, then laying the electrode on a plane
glass surface and rubbing with the rounded end of a glass rod.
The property of hydrogen in presence of colloidal platinum to
reduce is inherently connected with the relative magnitude of the
surface of the colloidal particles, if the particles be exceedingly
minute then the surface becomes very great and this is reflected in
an enhanced catalytic activity. A coating of such particles would
be unsuitable on electrodes for use in solutions in contact with
air or containing reducible substances. Suitable deposits can,
however, be obtained, which are sufficiently catalytically active
to produce sensitive and accurate hydrogen electrodes but which
will effect reduction only after some time has elapsed, as the author
was able to demonstrate in an extreme case in which the hydrogen
did not immediately reduce free chromic acid.

The catalytic reducing power of an electrode is often a question of the pH of the liquid.   Thus, although it was only in comparatively few cases that the author was able to prepare electrodes which, if they caused reduction at all, the rate at which it took place was so small that the hydrogen-ion concentrations of free chromic acid solutions could be measured before the error became perceptible, most of the good hydrogen electrodes prepared gave potentials corresponding to the true pH in dilute solutions of chromates when their pH values were greater than about 4 (*cf. J. Chem. Soc.*, 1926, 125).

It may be an advantage to discuss the behaviour of hydrogen electrodes when giving rise to reduction, as this may often occur especially in oxygenated biological fluids.   The behaviour of such hydrogen electrodes in free chromic acid solution may be taken as typical.   With the majority of electrodes no constant E.M.F. could be obtained, and the precise value at any moment appeared to depend on both the rate of passage of hydrogen through the electrode vessel and whether the electrode was partly or totally immersed in the solution.   Rapid passing of hydrogen effected rapid reduction, as indicated by the E.M.F. becoming less negative and even becoming positive, so much so that with a very plentiful supply of gas, the potential became of the same magnitude as that produced when a bright platinum electrode was substituted for the hydrogen electrode.   This reducing action was more pronounced when the hydrogen electrode was partly immersed.

Certain electrodes, saturated with hydrogen previous to immersion in chromic acid solutions, gave on complete immersion initial E.M.F's indicating hydrion concentrations equal to those calculated from conductivity data.   These E.M.F's slowly fell and the fall became much more rapid when the solution was agitated or the hydrogen turned on.   On stopping the hydrogen supply and allowing the solution to become quite still once again, the potential in some cases gradually rose to a true constant value. The hydrogen electrode has been used in the presence of other reducible ions.   F. L. Brown (*J. Amer. Chem. Soc.*, 1923, **45**, 297) measured hydrion concentrations in presence of ferric ions. He saturated several platinised platinum wire electrodes with hydrogen in vessels of the Hildebrand type and observed the E.M.F's immediately the electrodes were immersed.   By using several electrodes he was able to measure accurately the initial E.M.F. before reduction had commenced.

Previous saturation of hydrogen electrodes before immersion in the solution being investigated often renders pH measurements possible, and this is especially the case with biological liquids.

The position of the electrode with respect to the solution is a question of some importance. The catalytic activity of the hydrogen in the electrode is much more pronounced when the electrode is only partly immersed. In this connexion, reference may be made to the work of J. Eggert (*Z. Elektrochem.*, 1914, **20,** 370 ; 1915, **21,** 349). He investigated the velocity of absorption of hydrogen by platinised platinum and solutions of metallic salts at 17° C. He found that the reduction of ferric iron attained a maximum velocity when the platinum which served as catalyst was brought into contact with the hydrogen atmosphere above the solution. His results show that the maximum velocity of absorption is proportional to the surface of the platinum and the time during which it is in contact with the gas space, but independent of the number of times per minute the electrode was raised into the gas space and lowered into the solution. Under uniform conditions, the initial velocity of absorption of hydrogen is constant and independent of the nature of the solutes. As the reaction approaches completion, a decrease in the velocity occurs. Eggert interpreted the constancy of the initial velocity, which varied with the nature of the platinum black, as being due entirely to the occlusion process, and the second velocity which gradually fell off, to the activation by the platinum of the gas. Hydrogen is capable of distributing itself in platinised platinum and can exert a chemical influence in places other than the point of occlusion. He found, moreover, that electrolytically deposited platinum and palladium have practically the same activating power.

The author has always found that the best results are obtained by using foil which is as highly polished as possible, and then platinising from a 2 per cent. solution of platinic chloride containing a trace of lead acetate, 0·02 gram per 100 c.c., such that the surface of the platinum is only just covered. The voltage of the platinising circuit should be such that there is a vigorous evolution of gas, and the current should be reversed preferably every half-minute. Under these conditions platinisation should not take more than five minutes (*vide* Britton, *J. Chem. Soc.*, 1924, **125,** 1573 ; 1925, **127,** 2111). Any traces of chlorine left in the electrode can be removed by placing it in a dilute solution of sulphuric acid as cathode and electrolysing for half an hour.

There is probably no great benefit accruing from a reversal of the current every half-minute, and excellent electrodes have been prepared by electrolysis for two minutes without reversal. Although the presence of lead in the " black " layer is not absolutely necessary, it assists in providing a better covering, one which is adherent, and which has diminished reducing catalytic activity.

The reason why electrodes containing traces of lead are more satisfactory seems to be linked up with the greater size of the platinum black particles.

Limitations of the Hydrogen Electrode.

Because of this reducing action the hydrogen electrode has a limited use; though with some hydrogen electrodes these limitations are not so great as with others ; their success or failure being an inherent characteristic of the particular coating of the platinum black.   This failure can often be traced to either reduction, or absorption from solution of some gaseous product, such as ammonia or carbon dioxide.   As a rule, it cannot be used in presence of oxidising agents, such as nitrates, chlorates, permanganates, ferric salts, and substances capable of reduction, such as sulphur dioxide, sulphides and sulphur.   When used in presence of chromates care must be taken to guard against erroneous data. It cannot be used in presence of some organic compounds, especially those which are unsaturated, and certain amines and alkaloids.   The electrode behaves anomalously in presence of lead, cadmium, and univalent thallium salts, owing to reduction to kations of lower valency.   Salt solutions of metals more " noble " than hydrogen, namely, those metals whose normal electrode potentials are positive, $e.g.$, copper, silver, gold, render the electrode useless.   Sometimes the hydrogen electrode functions satisfactorily, even though reducible substances may be present. Thus, as already stated, the author was able to prepare electrodes which responded to changes in hydrogen-ion concentration in dilute chromic acid solutions, but as a rule, this is not the case.   Sometimes its application is restricted to a range of hydrogen-ion concentrations, as was found by the author ($J.$ $Chem. Soc.$, 1927, **147**) in the titration of an alkaline solution of tungstic acid, for when the hydrogen-ion concentration had become 10^{-4} reduction could be seen to be taking place.   The presence of nitrates and chromates when in weakly acid or alkaline solutions is very often without any disturbing effect on the electrode.   It is sometimes stated that the hydrogen electrode is sluggish and only attains equilibrium after some time has elapsed. This depends entirely upon the electrode itself—some, once having attained a state of equilibrium, for which 10 minutes are usually ample, are immediately and accurately responsive to both small and large changes in hydrion concentration.   Some become sluggish when being subjected to large and sudden changes.   The author recommends in all cases that before a hydrogen electrode

E.M.F. be taken as true, the same voltage within a millivolt should be given by at least one other electrode immersed in the same solution. It should also be mentioned, whereas a really satisfactory electrode gives identical results in both still and agitated solutions, that in general less reliable values are given when the solutions are still agitating, the latter tending to give E.M.F's which are a few millivolts too low. It is, of course, immaterial what form, whether foil or wire, of platinum electrode may be used in solutions which do not interfere with it, but for solutions containing reducible substances, wire electrodes will often be found unserviceable on account of the ease with which the hydrogen is discharged.

Much confusion has arisen over the precise conditions which are necessary for the preparation of really fool-proof electrodes. Although the author has used hydrogen electrodes extensively, he has endeavoured to be quite sure that each electrode was behaving satisfactorily, by using at least two good electrodes. Even by so doing, electrodes were obtained, which though they worked satisfactorily in solutions of moderate acidity or alkalinity, were not all that could be desired in solutions in the region of neutrality, and especially so, if those solutions were unbuffered. It seems certain that in the hands of inexperienced and unsuspecting workers, E.M.F's given by hydrogen electrodes often do not correspond to the true equilibrium conditions and consequently erroneous pH values are calculated. Many have been the explanations of, and excuses for, the unsatisfactory functioning of hydrogen electrodes, with the consequence that many are the methods which have been advocated for the preparation of satisfactory electrodes. Probably the conditions which are most conducive to the production of good electrodes involve the deposition of a very thin layer of fairly coarse particles of platinum black upon a highly polished platinum surface. Many workers have preferred to deposit the " black " upon gold surfaces, and they have usually attributed the sluggishness of the electrodes in which they used platinum, as base, to the possible diffusion of hydrogen through the black coating into the metal. It is well known that, whereas metallic platinum has the power to absorb hydrogen, gold does not absorb hydrogen. The sluggishness experienced with platinised platinum electrodes was therefore held to be due to the slower rate at which equilibrium was attained with the hydrogen which had passed beyond the " black " layer. Though this may have had some effect it seems more likely to have been more a question of the metallic surface, and

the superior surface of gold would account for certain workers'
preference for gold as the supporting medium. It is interesting
to recall that Böttger (*Z. physikal. Chem.*, 1897, 24, 251), who was
the first to carry out electrometric titrations with the hydrogen
electrode, found platinised platinum unsuited for the purpose,
and on the advice of Wilhelm Ostwald resorted to gold electrodes
coated with palladium black. Incidentally, Andrews (*J. Biol.
Chem.*, 1924, 50, 479) found that palladium black on platinum
gave less reliable electrodes than platinised platinum. Gold,
plated with palladium black, is also preferred by W. D. Treadwell
and Weiss (*Helv. Chim. Acta*, 1920, 2, 433). They state that for
titration work the ordinary platinum electrode required too much
time to come to equilibrium. Some workers have employed
gold-plated platinum electrodes covered with platinum or palladium
black. The gold plating is best carried out from a potassium
cyanide solution of auric oxide, which has been freshly precipi-
tated from gold chloride solution with a small quantity of am-
monium hydroxide and washed, and the cyanide solution boiled
until ammonia gas ceases to be evolved.

Another method of preparing platinised platinum electrodes,
in which an attempt was made to reduce the possibility of the
slow diffusion of hydrogen into the metal, was to deposit on a
glass surface, *e.g.*, a sealed glass tube, a continuous film of metallic
platinum by carefully heating after a solution of platinic chloride
and some organic reducing body had been uniformly applied.
Thus Westhaver (*Z. physikal. Chem.*, 1905, 51, 90) formed an
iridium film on glass with the aid of an alcohol flame and a mix-
ture prepared by dissolving 0·3 gram iridium chloride, which had
been moistened with concentrated hydrochloric acid, in 1 c.c. of
absolute alcohol saturated with boric acid, and then adding 1 c.c.
Venetian turpentine and 2 c.c. of lavender oil. In order to burn
platinum films on to the glass solutions of platinic chloride have
been used containing glycerin and also essence of camomile
(Gooch and Burdick, *Amer. J. Science*, 1912, 34, 107 ; Meillère,
J. pharm. chim., 1921, 21, 311).

Calculation of Hydrogen-Ion Concentration and the Meaning of pH.

It was shown in an earlier paragraph that the E.M.F. of the
hydrogen electrode with respect to a solution containing hydrogen-
ions was equal at 18° to 20° C. to 0·058 log [H˙]. Now the observed
E.M.F. of a cell is the difference between the E.M.F's of the two

electrodes, *i.e.*, E.M.F. observed

$$= E_{\text{N-calomel}} - E_{\text{hydrogen}}$$
$$= 0 \cdot 283 \quad - 0 \cdot 058 \log [\text{H}^{\cdot}]$$

Whence $\qquad \log [\text{H}^{\cdot}] = \dfrac{0 \cdot 283 \quad - \text{observed E.M.F.}}{0 \cdot 058}$

which for solutions containing less than one gram-molecule of hydrogen-ions per litre will be negative, and equal to $- x$ (say). Hence $[\text{H}^{\cdot}] = 10^{-x}$. x is the negative power of concentration to the base 10, and is spoken of as the pH value. It is therefore equal to

$$- \log [\text{H}^{\cdot}] \text{ or } \log \frac{1}{[\text{H}^{\cdot}]} ;$$

hence $\qquad p\text{H} = \dfrac{\text{observed E.M.F.} - \text{E.M.F. of calomel}}{0 \cdot 058}.$

To put it more clearly : pH $= 1$ corresponds to a concentration of 10^{-1} gram-hydrogen-ions per litre, or M/10,

$$p\text{H} = 2 \text{ to } \frac{\text{M}}{100}, p\text{H} = 10 \text{ to } 10^{-10}\text{M},$$

or M/10,000,000,000. To suggest that one is able to measure such an infinitesimally small concentration of hydrogen-ions appears to be ridiculous. The pH scale, however, does supply a useful and delicate scale of acidity and alkalinity, and it often happens that the adjustment of hydrogen-ion concentration to within narrow limits of this scale is the factor on which the success of a reaction may depend. Thus, for example, magnesium hydroxide cannot be precipitated until the hydrogen-ion concentration has been depressed to $10^{-10 \cdot 5}$, or pH $10 \cdot 5$ (*J. Chem. Soc.*, 1925, **127**, 2115).

Moreover, whatever may be the interpretation which eventually will be placed upon the voltages of hydrogen electrode, the pH hydrogen-ion concentration scale will probably remain an exceedingly convenient one, for it is one which permits of the correlation of true acidity, or alkalinity, as indicated by the colorimetric changes of indicators, and by other electrodes—all of which, in the first place have to be standardised against the hydrogen electrode. Failing such a scheme the acidity and alkalinity as obtained by either indicator or electrometric methods would have to be calculated in terms of potentials of hydrogen electrode. In a narrow sense, it may be held that this is all that is accomplished by the pH scale. Actually, it does considerably more, for as will be seen

in later chapters the hydrogen-ion concentration conception provides an excellent means of studying the ionisation and neutralisation of weak acids and bases. As mentioned before, it is in regard to the behaviour of strong electrolytes that the ion-concentration idea is far from satisfactory, and should the concept of ion-activity gain general acceptance, then the above pH scale will be superseded by a pH scale of hydrogen-ion activity ; values on which will differ slightly in magnitude from those on the present scale.

It now remains to show the relationship which these hydrogen-ion concentrations bear to acidity and alkalinity. Water dissociates electrolytically to an extremely small extent into hydrogen- and hydroxyl-ions. The product, K_w, of these concentrations [H˙] [OH′] for any particular temperature is a fixed quantity, and is termed the *ionic product of water*. At 18° C., $K_w = 10^{-14.13}$, and consequently, when pure water dissociates $H_2O \rightleftharpoons H˙ + OH′$ into equal quantities of hydrogen- and hydroxyl-ions [H˙] = [OH′], and therefore $[H˙]^2 = 10^{-14.13}$, or $[H˙] = 10^{-7.1}$. This means that at 18° C. exact neutrality corresponds to a hydrion concentration of $10^{-7.1}$ or pH 7·1. The hydroxyl-ion concentration of a solution of pH 10 (say), i.e. $[H˙] = 10^{-10}$, and therefore $[OH′] = 10^{-14.2}/10^{-10} = 10^{-4.2}$. Solutions are acid up to pH 7·1, and above, alkaline.

Fig. 4 explains the origin of the E.M.F. of the cell in a somewhat clearer way. The positive E.M.F's of the various calomel electrodes are shown above the arbitrary zero potential, *viz.*, E of H_2/H˙ (1 gram-mol. per litre) = 0, and the varying negative E.M.F's of the hydrogen electrode in solutions containing less than 1 gram-mol. of hydrogen ion per litre, below. The concentrations of ions corresponding to the various voltages of the hydrogen electrode alone were calculated from $E_h = 0.058 \log [H˙]$. Thus the arrows showing a P.D. of 0·783 volt (say) between the N-calomel electrode and hydrogen electrode immersed in a solution whose hydrion concentration is $10^{-8.62} = 2.4 \times 10^{-9}$ or pH = 8·62, indicate that − 0·500 volt was due to the hydrogen electrode from which these concentrations were found.

Ionic Product of Water.

In the foregoing calculations we had occasion to consider the *ionic product of water*, and as this constant is of fundamental importance in the quantitative study of acidity and alkalinity we shall now accord it some discussion. It is the outcome of the application of the law of mass action to the electrolytic dissociation of

pure water; thus, the equation $H_2O \rightleftharpoons H^{\cdot\cdot} + OH'$ represents the main course of the dissociation of water—there is also an infinitesimally small concentration of oxygen-ions, O'', but as we
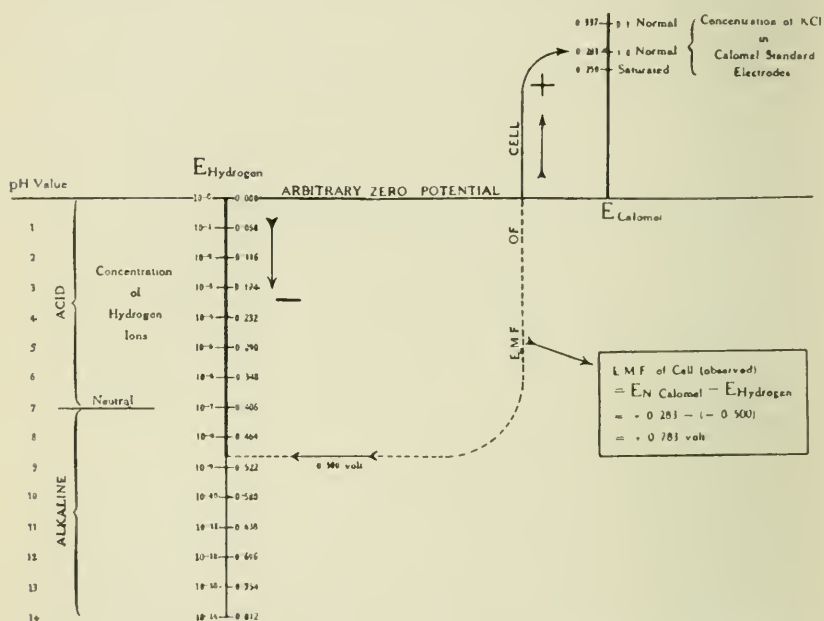
FIG. 4.— Variation in E.M.F. of Hydrogen-Calomel Cell with Hydrogen-ion Concentration at 18° to 20° C.

shall see in a later chapter the further dissociation of the hydroxyl-ions necessary to produce them is so small as to be without any practical significance here—and therefore on the grounds of the mass law

$$\frac{[H^{\cdot}] \times [OH']}{[H_2O]} = K,$$

whence $\qquad K_w = K \times [H_2O] = [H^{\cdot}][OH'],$

for the concentration of undissociated water can, in comparison with the extremely small portion which undergoes ionisation, be regarded as constant. Hence the constant, K_w, known as the ionic product of water, is equal to the true dissociation constant

of water multiplied by the concentration of water in a litre, *viz.*, 1000/18 gram-molecules.

Values of K_w have been found in a variety of ways, the more important being those based on conductivity and electromotive force measurements. Kohlrausch and Heydweiller found the specific conductivity of pure water to be 0.0384×10^{-6} r.o's at $18°$ C. In pure water the concentrations of hydrogen-ions and of hydroxyl-ions are equal, and therefore

$$0.0384 \times 10^{-6} = n\,(l_{H^.} + l_{OH'}).$$

Knowing that the ionic mobility of the hydrogen-ion, $l_{H^.} = 314$, and $l_{OH'}$, that of the hydroxyl-ion is 174, and therefore the number of each ion, n, in 1 c.c. of water is given by

$$0.0384 \times 10^{-6} = n\,(314 + 174),$$

we find that $n = 7.86 \times 10^{-9}$.

Hence the number of $H^.$-ions in 1 litre, *i.e.*, $[H^.]$, also the number of OH' ions, $[OH']$, is

$$1000 \times 7.86 \times 10^{-9} = 7.86 \times 10^{-6},$$

and therefore

$$K_w = (7.86 \times 10^{-6})^2 = 0.62 \times 10^{-14} = 10^{-11.21}.$$

The ionisation of water, though very small, is affected by temperature changes to a marked extent. The reason for this can be seen from calculations based on the van't Hoff isochore. It has been found experimentally that the neutralisation of strong acids by strong bases, *e.g.*, HCl, HNO_3, KOH and NaOH, at $20°$ C. results in the production of 13,700 calories when gram-equivalents of the acid and alkali are employed. In such cases the heat evolved happens to be the heat of ionisation, thus $H^.$ $+ OH' = H_2O$, of water, and can therefore be substituted for U in the van't Hoff isochore, in order to calculate the variation in K_w which would be expected to occur for temperatures in the region of $20°$ C. (*i.e.*, $293°$ A.).

Hence

$$\frac{d\log_{10} K_w}{dT} = -\frac{U}{2.303 \times R \times T^2} = -\frac{13700}{2.303 \times 1.988 \times (298)^2}$$
$$= -0.0349,$$

where the factor 2.303 is introduced to convert the expression from hyperbolic to common logarithms and 1.988 is R in calories per degree. The negative value of the expression, -0.0349,

indicates that the formation of water from its ions has an increasing tendency not to reach completion, *i.e.*, in forming undissociated water molecules, with rise in temperature. In other words, increased electrolytic dissociation into hydrogen- and hydroxylions occurs with rise in temperature. Hence, we should expect K_w to increase in magnitude with rise in temperature. The calculation would suggest that the negative index would become more positive by 0·0349 per degree. The average of practical values obtained from 16° to 26° C. show that the actual increment per degree is 0·0340. This will be seen from the following table, which gives the values of K_w and pK_w, *i.e.*, the negative exponent of K_w to the base 10, for temperatures from 16° to 40° C. They are taken from Michaelis' *Die Wasserstoffionen-Konzentration*, 1922, p. 23 :—

TABLE 3.

Temperature °C.	$K_w \times 10^{14}$.	pK_w.
16	0·63	14·20
17	0·68	14·17
18	0·74	14·13
19	0·79	14·10
20	0·86	14·07
21	0·93	14·03
22	1·01	14·00
23	1·10	13·96
24	1·19	13·93
25	1·27	13·90
26	1·38	13·86
27	1·50	13·83
28	1·62	13·79
29	1·76	13·76
30	1·89	13·73
31	2·04	13·69
32	2·19	13·66
33	2·35	13·63
34	2·51	13·60
35	2·71	13·57
36	2·92	13·54
37	3·13	13·51
38	3·35	13·48
39	3·59	13·45
40	3·80	13·42

These figures show that temperature has an appreciable effect on K_w and therefore upon the hydrogen-ion concentrations corresponding to true neutrality at different temperatures. Thus at neutrality $[H^\cdot] = [OH']$, and therefore $[H^\cdot]^2 = K_w$ or

$$[H^\cdot] = \sqrt{K_w} = \sqrt{10^{-pK_w}} = 10^{-\frac{pK_w}{2}}.$$

Hence from the above table we see that [H˙] at neutrality at 16° C. is $10^{-7.10}$ and becomes $10^{-6.71}$ at 40° C. These negative indices are usually referred to as the pH value in the case of hydrogen-ion concentrations. In other words the hydrogen-ion concentration has a pH value of $\frac{1}{2}$ $p\mathrm{K}_w$ at neutrality. Some experimental values of $p\mathrm{K}_w$ at more removed temperatures show that at 0° C. $p\mathrm{K}_w = 14.94$, and at 100° C. $p\mathrm{K}_w = 12.24$. For a fuller discussion of the many methods by which K_w has been found the student is referred to Lewis's *Text-Book of Physical Chemistry*.

Actual Number of Hydrogen-Ions in Water.

Although in the measurement of acidity we do not concern ourselves with the actual number of hydrogen-ions present, but merely with their concentration *expressed in terms of gram-ions or gram-molecules*, it is not without interest to consider for a moment the numbers of ions which produce the changes in acidity. One gram-molecule of any gas contains 6.06×10^{23} molecules. This value is the so-called Avogadro number, and is the direct result of Avogadro hypothesis. The precise value given is probably accurate within 0.1 per cent. and is based on Millikan's determination of the electronic charge. Now we see from the previous paragraph that at ordinary temperatures, $\mathrm{K}_w = 10^{-14}$ (approx.), therefore in pure water the concentration of hydrogen-ions, [H˙] is equal to that of hydroxyl-ions, [OH′], and consequently each is equal to 10^{-7} gram-mols. of ions per litre. Such a concentration of ions appears therefore to be composed of $10^{-7} \times 6.06 \times 10^{23} = 6.06 \times 10^{16}$ hydrogen- or hydroxyl-ions, as the case may be, and these are contained in 1 litre of water. But 1 litre of water contains $1000/18$ gram-mols. of water, each of which comprises 6.06×10^{23} molecules, and therefore the actual number of molecules of water in 1 litre

$$= \frac{1000}{18} \times 6.06 \times 10^{23}$$

$$= 337 \times 10^{23} \text{ molecules of } H_2O.$$

From these 6.06×10^{16} hydrogen-ions and 6.06×10^{16} hydroxyl-ions are formed. Hence out of 337×10^{23} water molecules 6.06×10^{16} are electrolytically dissociated, and therefore of 556 million water molecules only one is ionised.

pH Values.

We have seen that the potential of a hydrogen electrode, compared with the normal hydrogen electrode as being of zero potential, may be expressed by the following formula :—

$$E_{H_2} = 0.0001984 \; T \log [H^{\bullet}]$$

and therefore,

$$pH = - \log [H^{\bullet}] = \log \frac{1}{[H^{\bullet}]} = \frac{- E_{H_2}}{0.0001984 \; T}$$

consequently at $18°$ to $20°$ C.,

$$pH = - \frac{E_{H_2}}{0.058}.$$

In view of the fact that for any particular temperature the product of the concentrations of hydrogen-ions and of hydroxyl-ions in any aqueous solution is of constant value, namely, K_w, we find that if the hydrogen-ion concentration be known then the hydroxyl-ion concentration can be easily calculated. Moreover we are provided with a scheme by which the gradual transition of the reaction of a solution from acidity to alkalinity can be quantitatively mapped out in terms of decreasing hydrogen-ion concentrations, $i.e.$, increasing pH values, or in terms of increasing hydroxyl-ion concentrations, $i.e.$, decreasing pOH values. If we take the ionic product of water, K_w, to be equal to 10^{-14} at ordinary temperatures, we find that the hydroxyl-ion concentration of a solution containing one gram-mol. of hydrogen-ions per litre, $i.e.$, $1M - H^{\bullet}$ or $1N - H^{\bullet}$, is equal to $K_w/[H^{\bullet}] = 10^{-14}$ gram-mols. of hydroxyl-ion per litre. Similarly in a solution decinormal with respect to hydrogen-ions contains 10^{-13} gram-mols. of hydroxyl-ions per litre, and on the other hand, a solution decinormal with respect to hydroxyl-ions will contain 10^{-13} gram-mols. of hydrogen-ions. If we represent the negative exponent to the base 10 of hydroxyl-ion concentrations by the symbol pOH, and the negative index of the ionic product by pK_w, then

$$pK_w = pH + pOH.$$

As stated on page 39, true neutrality occurs when

$$pH = pOH = \tfrac{1}{2} pK_w = 7,$$

and therefore pH 0 to pH 7, or pOH 14 to pOH 7 represents the range of diminishing acidity, and pH 7 to pH 14, or pOH 7 to pOH 0

corresponds to the range of increasing alkalinity at ordinary temperatures. In general, however, the different degrees of acidity are from pH 0 to pH $= \frac{1}{2} p\mathrm{K}_w$, or, pOH $= p\mathrm{K}_w$ to pH $= \frac{1}{2} p\mathrm{K}_w$; and alkalinity, from pH $= \frac{1}{2} p\mathrm{K}_w$ to pH $= 14$, or, pOH $= \frac{1}{2} p\mathrm{K}_w$ to pOH $= 0$. Of course in concentrated acid solutions the concentration of hydrogen-ions will be greater than 1 molar, whence pH becomes negative, say $-x$, and therefore pOH $= 14 + x$ at ordinary temperatures, and similarly for alkaline solutions containing greater concentrations of hydroxyl-ions than 1 M, pOH $= -x$, whence pH $= 14 + x$.

In Table 4 there is set out these hydrogen- and hydroxylion concentrations, their respective pH or pOH values, and the

TABLE 4.

VARIATIONS IN E.M.F. OF HYDROGEN AND QUINHYDRONE ELECTRODES WITH pH.

[H·].		[OH′].	pH.	pOH.	E.M.F. of Hydrogen Electrode against			E.M.F. of Quinhydrone Electrode against	
					Arb. Zero (N-Hyd.).	N-Calomel.	Sat. Cal.	Arb. Zero (N-Hyd.).	N-Calomel.
Acidity	$1 (10^\circ)$	10^{-14}	0	14	0.000	-0.283	-0.250	$+0.704$	$+0.421$
	10^{-1}	10^{-13}	1	13	-0.058	-0.341	-0.308	$+0.646$	$+0.363$
	10^{-2}	10^{-12}	2	12	-0.116	-0.399	-0.366	$+0.588$	$+0.305$
	10^{-3}	10^{-11}	3	11	-0.174	-0.457	-0.424	$+0.530$	$+0.247$
	10^{-4}	10^{-10}	4	10	-0.232	-0.515	-0.482	$+0.472$	$+0.189$
	10^{-5}	10^{-9}	5	9	-0.290	-0.573	-0.540	$+0.414$	$+0.131$
	10^{-6}	10^{-8}	6	8	-0.348	-0.631	-0.598	$+0.356$	$+0.073$
Neutrality	10^{-7}	10^{-7}	7	7	-0.406	-0.689	-0.656	$+0.298$	$+0.015$
Alkalinity	10^{-8}	10^{-6}	8	6	-0.464	-0.747	-0.714	$+0.240$	-0.043
	10^{-9}	10^{-5}	9	5	-0.522	-0.805	-0.772	$+0.180$	-0.101
	10^{-10}	10^{-4}	10	4	-0.580	-0.863	-0.830		
	10^{-11}	10^{-3}	11	3	-0.638	-0.921	-0.888		
	10^{-12}	10^{-2}	12	2	-0.696	-0.979	-0.946		
	10^{-13}	10^{-1}	13	1	-0.754	-1.037	-1.004		
	10^{-14}	$1(10^\circ)$	14	0	-0.812	-1.095	-1.062		

E.M.F's of hydrogen and quinhydrone electrodes, to which they give rise, both referred to the normal hydrogen electrode as arbitrary zero, and also to the normal calomel electrode. The voltages of the hydrogen-electrode are also compared with that of the saturated calomel electrode. These figures were calculated for temperatures 18° to 20° C. from the formulæ

$$E_{H_2} = 0.058 \log [\mathrm{H}\cdot]$$

and $\quad E_{\text{observed}} = E_{\text{calomel}} - E_{H_2},$

denoting the E.M.F. produced when the hydrogen electrode is incorporated in a cell, the other pole of which is a standard calomel. It will be seen that with each increasing pH unit, the E.M.F. of both the hydrogen and the quinhydrone (see later) electrodes become more negative or smaller by 58 millivolts, as will be understood from the formula.

TABLE 5.

HYDROGEN-ION CONCENTRATIONS CORRESPONDING TO pH $n \cdot 00$—pH $(n + 1) \cdot 00$.

pH.	[H·].	pH.	[H·].	pH.	[H·].
$n \cdot 00$	$1 \cdot 00 \times 10^{-n}$	$n \cdot 34$	$0 \cdot 46 \times 10^{-n}$	$n \cdot 68$	$0 \cdot 21 \times 10^{-n}$
$n \cdot 01$	$0 \cdot 98 \times 10^{-n}$	$n \cdot 35$	$0 \cdot 45 \times 10^{-n}$	$n \cdot 69$	$0 \cdot 20 \times 10^{-n}$
$n \cdot 02$	$0 \cdot 96 \times 10^{-n}$	$n \cdot 36$	$0 \cdot 44 \times 10^{-n}$	$n \cdot 70$	$0 \cdot 20 \times 10^{-n}$
$n \cdot 03$	$0 \cdot 93 \times 10^{-n}$	$n \cdot 37$	$0 \cdot 43 \times 10^{-n}$	$n \cdot 71$	$0 \cdot 20 \times 10^{-n}$
$n \cdot 04$	$0 \cdot 91 \times 10^{-n}$	$n \cdot 38$	$0 \cdot 42 \times 10^{-n}$	$n \cdot 72$	$0 \cdot 19 \times 10^{-n}$
$n \cdot 05$	$0 \cdot 89 \times 10^{-n}$	$n \cdot 39$	$0 \cdot 41 \times 10^{-n}$	$n \cdot 73$	$0 \cdot 18 \times 10^{-n}$
$n \cdot 06$	$0 \cdot 87 \times 10^{-n}$	$n \cdot 40$	$0 \cdot 40 \times 10^{-n}$	$n \cdot 74$	$0 \cdot 18 \times 10^{-n}$
$n \cdot 07$	$0 \cdot 85 \times 10^{-n}$	$n \cdot 41$	$0 \cdot 39 \times 10^{-n}$	$n \cdot 75$	$0 \cdot 18 \times 10^{-n}$
$n \cdot 08$	$0 \cdot 83 \times 10^{-n}$	$n \cdot 42$	$0 \cdot 38 \times 10^{-n}$	$n \cdot 76$	$0 \cdot 17 \times 10^{-n}$
$n \cdot 09$	$0 \cdot 81 \times 10^{-n}$	$n \cdot 43$	$0 \cdot 37 \times 10^{-n}$	$n \cdot 77$	$0 \cdot 17 \times 10^{-n}$
$n \cdot 10$	$0 \cdot 80 \times 10^{-n}$	$n \cdot 44$	$0 \cdot 36 \times 10^{-n}$	$n \cdot 78$	$0 \cdot 17 \times 10^{-n}$
$n \cdot 11$	$0 \cdot 78 \times 10^{-n}$	$n \cdot 45$	$0 \cdot 35 \times 10^{-n}$	$n \cdot 79$	$0 \cdot 16 \times 10^{-n}$
$n \cdot 12$	$0 \cdot 76 \times 10^{-n}$	$n \cdot 46$	$0 \cdot 35 \times 10^{-n}$	$n \cdot 80$	$0 \cdot 16 \times 10^{-n}$
$n \cdot 13$	$0 \cdot 74 \times 10^{-n}$	$n \cdot 47$	$0 \cdot 34 \times 10^{-n}$	$n \cdot 81$	$0 \cdot 15 \times 10^{-n}$
$n \cdot 14$	$0 \cdot 73 \times 10^{-n}$	$n \cdot 48$	$0 \cdot 33 \times 10^{-n}$	$n \cdot 82$	$0 \cdot 15 \times 10^{-n}$
$n \cdot 15$	$0 \cdot 71 \times 10^{-n}$	$n \cdot 49$	$0 \cdot 32 \times 10^{-n}$	$n \cdot 83$	$0 \cdot 15 \times 10^{-n}$
$n \cdot 16$	$0 \cdot 69 \times 10^{-n}$	$n \cdot 50$	$0 \cdot 32 \times 10^{-n}$	$n \cdot 84$	$0 \cdot 14 \times 10^{-n}$
$n \cdot 17$	$0 \cdot 68 \times 10^{-n}$	$n \cdot 51$	$0 \cdot 31 \times 10^{-n}$	$n \cdot 85$	$0 \cdot 14 \times 10^{-n}$
$n \cdot 18$	$0 \cdot 66 \times 10^{-n}$	$n \cdot 52$	$0 \cdot 30 \times 10^{-n}$	$n \cdot 86$	$0 \cdot 14 \times 10^{-n}$
$n \cdot 19$	$0 \cdot 65 \times 10^{-n}$	$n \cdot 53$	$0 \cdot 30 \times 10^{-n}$	$n \cdot 87$	$0 \cdot 13 \times 10^{-n}$
$n \cdot 20$	$0 \cdot 63 \times 10^{-n}$	$n \cdot 54$	$0 \cdot 29 \times 10^{-n}$	$n \cdot 88$	$0 \cdot 13 \times 10^{-n}$
$n \cdot 21$	$0 \cdot 62 \times 10^{-n}$	$n \cdot 55$	$0 \cdot 28 \times 10^{-n}$	$n \cdot 89$	$0 \cdot 13 \times 10^{-n}$
$n \cdot 22$	$0 \cdot 60 \times 10^{-n}$	$n \cdot 56$	$0 \cdot 28 \times 10^{-n}$	$n \cdot 90$	$0 \cdot 13 \times 10^{-n}$
$n \cdot 23$	$0 \cdot 59 \times 10^{-n}$	$n \cdot 57$	$0 \cdot 27 \times 10^{-n}$	$n \cdot 91$	$0 \cdot 12 \times 10^{-n}$
$n \cdot 24$	$0 \cdot 58 \times 10^{-n}$	$n \cdot 58$	$0 \cdot 26 \times 10^{-n}$	$n \cdot 92$	$0 \cdot 12 \times 10^{-n}$
$n \cdot 25$	$0 \cdot 56 \times 10^{-n}$	$n \cdot 59$	$0 \cdot 26 \times 10^{-n}$	$n \cdot 93$	$0 \cdot 12 \times 10^{-n}$
$n \cdot 26$	$0 \cdot 55 \times 10^{-n}$	$n \cdot 60$	$0 \cdot 25 \times 10^{-n}$	$n \cdot 94$	$0 \cdot 12 \times 10^{-n}$
$n \cdot 27$	$0 \cdot 54 \times 10^{-n}$	$n \cdot 61$	$0 \cdot 25 \times 10^{-n}$	$n \cdot 95$	$0 \cdot 11 \times 10^{-n}$
$n \cdot 28$	$0 \cdot 53 \times 10^{-n}$	$n \cdot 62$	$0 \cdot 24 \times 10^{-n}$	$n \cdot 96$	$0 \cdot 11 \times 10^{-n}$
$n \cdot 29$	$0 \cdot 51 \times 10^{-n}$	$n \cdot 63$	$0 \cdot 23 \times 10^{-n}$	$n \cdot 97$	$0 \cdot 11 \times 10^{-n}$
$n \cdot 30$	$0 \cdot 50 \times 10^{-n}$	$n \cdot 64$	$0 \cdot 23 \times 10^{-n}$	$n \cdot 98$	$0 \cdot 11 \times 10^{-n}$
$n \cdot 31$	$0 \cdot 49 \times 10^{-n}$	$n \cdot 65$	$0 \cdot 22 \times 10^{-n}$	$n \cdot 99$	$0 \cdot 10 \times 10^{-n}$
$n \cdot 32$	$0 \cdot 48 \times 10^{-n}$	$n \cdot 66$	$0 \cdot 22 \times 10^{-n}$	$n + 1 \cdot 00$	$0 \cdot 10 \times 10^{-n}$
$n \cdot 33$	$0 \cdot 47 \times 10^{-n}$	$n \cdot 67$	$0 \cdot 21 \times 10^{-n}$		

It should always be remembered that the pH notation is merely a convenient method for the representation of hydrogen-ion concentrations, which are related to one another by the equation

$$[H \cdot] = 10^{-p\mathrm{H}}.$$

Very often the pH scale of acidity is compared with a thermometric scale of temperature. The analogy is superficial, for each unit of increase in the pH value corresponds to a diminution in hydrogen-ion concentration by one-tenth of that concentration indicated by the preceding pH value—in other words, the pH scale represents the hydrion concentrations given by the terms of a geometrical progression whose first term is 1 and the ratio, $\frac{1}{10}$. Moreover, this is true of the tenth and hundredth divisions of each individual
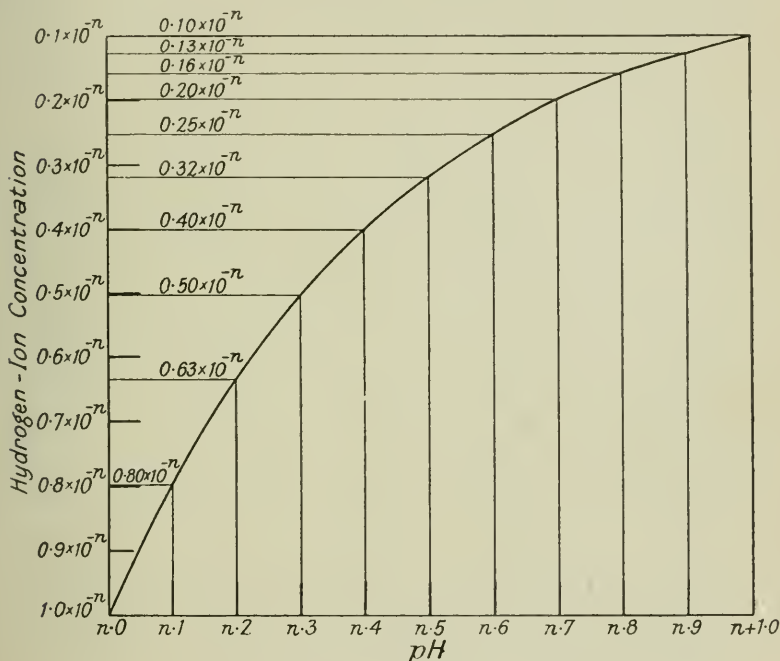

FIG. 5.—Relationship between pH and Hydrogen-Ion Concentration.

pH unit. In Table 5 are given the hydrogen-ion concentrations corresponding to pH values, $n\cdot00$ to $n + 1\cdot00$, where n is any pH integer.

These data are plotted in Fig. 5. They show that each succeeding tenth division of a pH unit represents differing and increasingly smaller decreases in the concentration of hydrogen-ions. Thus, it happens that an increase of $0\cdot5$ pH unit from pH $n\cdot0$ to pH $n\cdot5$ refers to a fall in hydrion concentration of 68 per cent. of the concentration at pH n, whereas the increase of a further $0\cdot5$ pH unit from pH $n\cdot5$ to pH $n + 1\cdot0$ brings about a diminution of less than a third of that amount, namely, 22 per cent.

Table 6 gives examples of the hydrogen- and hydroxyl-ion concentrations, together with their pH and pOH values of certain acids and bases in different dilutions at 18° C. The pOH values and hydroxyl-ion concentrations were derived from pK$_w$ = 14·13 (Table No. 3).

TABLE 6.

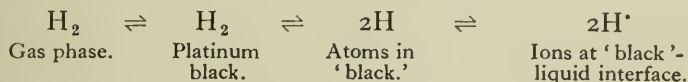### HYDROGEN-ION CONCENTRATIONS AND pH VALUES OF ACIDS AND BASES.

Electrolyte.	[H˙].	pH.	[OH′].	pOH.
N-HCl . . .	$8·0 \times 10^{-1}$	0·10	$9·3 \times 10^{-15}$	14·03
0·1 N-HCl . .	$8·5 \times 10^{-2}$	1·07	$8·7 \times 10^{-14}$	13·06
0·01 N-HCl . .	$9·6 \times 10^{-3}$	2·02	$7·8 \times 10^{-13}$	12·11
0·001 N-HCl . .	$9·8 \times 10^{-4}$	3·01	$7·6 \times 10^{-12}$	11·12
0·0001 N-HCl . .	$9·8 \times 10^{-5}$	4·01	$7·6 \times 10^{-11}$	10·12
N-CH$_3$COOH . .	$4·3 \times 10^{-3}$	2·37	$1·7 \times 10^{-12}$	11·76
0·1 N-CH$_3$COOH .	$1·3 \times 10^{-3}$	2·87	$5·5 \times 10^{-12}$	11·26
0·01 N-CH$_3$COOH .	$4·3 \times 10^{-4}$	3·37	$1·7 \times 10^{-11}$	10·76
0·001 N-CH$_3$COOH .	$1·3 \times 10^{-4}$	3·87	$5·5 \times 10^{-11}$	10·26
0·1 N-H$_2$SO$_4$ . .	$5·9 \times 10^{-2}$	1·23	$1·3 \times 10^{-13}$	12·90
N-NaOH . . .	$8·9 \times 10^{-15}$	14·05	$8·3 \times 10^{-1}$	0·08
0·1 N-NaOH . .	$8·5 \times 10^{-14}$	13·07	$8·7 \times 10^{-2}$	1·06
0·01 N-NaOH . .	$7·6 \times 10^{-13}$	12·12	$9·8 \times 10^{-3}$	2·01
0·001 N-NaOH .	$7·4 \times 10^{-12}$	11·13	$1·0 \times 10^{-3}$	3·00
N-NH$_4$OH . .	$1·7 \times 10^{-12}$	11·77	$4·4 \times 10^{-3}$	2·36
0·1 N-NH$_4$OH . .	$5·4 \times 10^{-12}$	11·27	$1·4 \times 10^{-3}$	2·86
0·01 N-NH$_4$OH .	$1·7 \times 10^{-11}$	10·77	$4·4 \times 10^{-4}$	3·36
0·001 N-NH$_4$OH .	$5·4 \times 10^{-11}$	10·27	$1·4 \times 10^{-4}$	3·86

Corrections to be Applied to Hydrogen Electrode E.M.F. Measurements for Aqueous Vapour Pressure and Variations in Atmospheric Pressure.

In our discussions on page 8 of the mathematical interpretations which are placed upon the potentials existing between a metal and a solution, we postulated the existence of electrolytic solution pressure acting at the electrode surface and urging atoms into solution in the ionic condition. This pressure was believed to be counteracted by the osmotic pressure of the same ions which were already in solution through the dissociation of a salt. Thus, if P be the electrolytic solution pressure and p the osmotic pressure of the cations, then

$$ E = \frac{RT}{F} \log_e \frac{p}{P}. $$

In the case of a metal electrode this electrolytic solution pressure is an intrinsic property of the metal, whereas with gas electrodes it is regarded as dependent upon the pressure of the gas surrounding the absorbing electrode. Thus at the interface of hydrogen gas and platinum black, an equilibrium is set up between the molecules of hydrogen and the molecules of gas absorbed by the 'black,' and these in turn enter into equilibrium with atoms which are supposed to exist therein, a proportion of which automatically become ionised through the catalysing action of the finely divided platinum. This series of equilibria may be represented schematically :—

$$\underset{\text{Gas phase.}}{H_2} \quad \rightleftharpoons \quad \underset{\substack{\text{Platinum} \\ \text{black.}}}{H_2} \quad \rightleftharpoons \quad \underset{\substack{\text{Atoms in} \\ \text{'black.'}}}{2H} \quad \rightleftharpoons \quad \underset{\substack{\text{Ions at 'black'-} \\ \text{liquid interface.}}}{2H^{\cdot}}$$

If these equilibria are all interdependent, then the pressure of the hydrogen surrounding the electrode may be expected to have some influence upon the electromotive activity of the hydrogen electrode. For ordinary routine work errors from this source will generally be of negligible dimensions, but as such errors are produced, they must be taken into account in the case of hydrogen electrode measurements of a high degree of precision and therefore will here be considered. If hydrogen be passed through the electrode vessel very slowly then the pressure inside the vessel will be equal to that of the atmosphere, with the exception that the gas after bubbling slowly through an aqueous solution into the gas space will have become saturated, or very nearly so, with water vapour. The pressure of hydrogen in contact with the electrode will be partial and will be equal to the atmospheric pressure, as indicated by the barometer less that of water vapour required to saturated air at the temperature at which the experiment is being performed.

In order to evaluate the correction involved in working at hydrogen pressures other than 1 atmosphere, 760 mm. mercury pressure, we shall consider the E.M.F. of cell in which two hydrogen electrodes dip into the same solution ; the pressures of the hydrogen surrounding the two electrodes being π_1 and π_2 atmospheres, giving rise to the respective electrolytic solution pressures, P_1 and P_2 and therefore to the individual electrode potentials E_1 and E_2 respectively, with regard to the solution. Now, we see from the above expression that if $P_1 > P_2$, then $E_2 > E_1$, and conversely, if $P_1 < P_2$, then $E_2 < E_1$. The E.M.F. of the cell comprises the difference $E_2 - E_1$ in the first instance, and $E_1 - E_2$ in the second.

Hence, if $E_2 > E_1$

$$
\begin{aligned}
\text{E.M.F.}_{\text{(observed)}} &= E_2 - E_1 \\
&= \frac{RT}{F} \log_e \frac{p}{P_2} - \frac{RT}{F} \log_e \frac{p}{P_1} \\
&= \frac{RT}{F} \log_e \frac{P_1}{P_2}.
\end{aligned}
$$

Now $\qquad \dfrac{[H^{\cdot}]}{[H]} = k_1,$ and $\underset{\text{(in black)}}{H_2 \rightleftharpoons 2H}$

$$
\therefore \frac{[H]^2}{[H_2]_{\text{(black)}}} = k_2,
$$

and $\qquad \underset{\text{gas} \quad \text{(in black)}}{H_2 \rightleftharpoons H_2}, \qquad \therefore \dfrac{[H_2]_{\text{black}}}{[H_2]_{\text{gas}}} = k_3,$

we find that $\qquad [H^{\cdot}]^2 = \dfrac{k_1 k_3}{k_2}[H_2]_{\text{gas}},$

$$
i.e., [H^{\cdot}] = \sqrt{K[H_2]_{\text{gas}}}, \quad \text{or} \quad P = \sqrt{K \cdot \pi}.
$$

As each of the above quantities expressed in square brackets refer to pressures of hydrogen in either the molecular, atomic or ionic state, we find that the electrolytic solution pressure, $i.e.$, $P = [H^{\cdot}]$ is proportional to the square root of the pressure of the hydrogen gas in the electrode vessel $= \pi$. Hence the observed

$$
\begin{aligned}
\text{E.M.F.} = E_2 - E_1 &= \frac{RT}{F} \log_e \frac{P_1}{P_2} \\
&= \frac{RT}{F} \log_e \frac{\sqrt{K} \cdot \sqrt{\pi_1}}{\sqrt{K} \cdot \sqrt{\pi_2}} = \frac{RT}{2F} \log_e \frac{\pi_1}{\pi_2},
\end{aligned}
$$

and therefore if E_1 be produced by a hydrogen electrode with hydrogen pressure equal to 1 atmosphere, and E_2 the potential set up by another hydrogen electrode, whose hydrogen pressure is π atmospheres, both immersed in the same solution, then the difference in potential between these two electrodes gives the correction which should be applied to measurements performed with a hydrogen electrode not served with hydrogen at exactly atmospheric pressure. The correction is thus

$$
\begin{aligned}
E_{\text{pressure}} &= \frac{RT}{2F} \log_e \frac{1}{\pi} \\
&= \frac{0 \cdot 0001984T}{2} \log_{10} \frac{1}{\pi} \\
&= 0 \cdot 0000992T \log \frac{1}{\pi}.
\end{aligned}
$$

When π is less than 1, then E is positive ; and negative when π is greater than atmospheric pressure. We may therefore write down that

$$\mathrm{E_{pressure} = E_{uncorrected} - E_{corrected}}$$

and therefore

$$\mathrm{E_{uncorrected} = E_{corrected} + E_{pressure}}$$

Hence the P.D's between a hydrogen electrode at pressure π and a standard calomel electrode are equal to

$$
\begin{aligned}
\mathrm{E.M.F._{cell}} &= \mathrm{E_{calomel} - E_{H_2\ (uncorrected)}} \\
&= \mathrm{E_{calomel} - (E_{H_2\ (corrected)} + E_{pressure})} \\
&= \mathrm{E_{calomel} - E_{H_2\ (corrected)} - E_{pressure}} \\
&= \mathrm{E_{calomel} - 0 \cdot 0001984 T \log [H^{\cdot}] - 0 \cdot 0000992 T \log \frac{1}{\pi}}
\end{aligned}
$$

whence

$$
p\mathrm{H} = \frac{\mathrm{E.M.F._{cell} - E_{calomel} + 0 \cdot 0000992 T \log \frac{1}{\pi}}}{0 \cdot 0001984 T}.
$$

The standard atmospheric pressure is that which produces a downward pressure on a square cm. of a column of 760 mm. mercury in height when measured at 0° C. On account of the expansion which mercury undergoes with temperature, it is evident that this column will increase in height, and consequently a pressure equal to 760 mm. mercury at 0° C. will be produced a column slightly higher at a higher temperature. Strictly speaking, therefore, all barometric heights should be corrected for expansion in order to make them comparable. In hydrogen electrode measurements the error involved in omitting this correction is usually much less than 1 millivolt. Another point to remember is that this so-called unit atmospheric pressure refers only to the latitude 45° where the 1 gram weight is equal to a force of 980·6 dynes, thus defining the unit atmosphere in absolute units as $76 \times 13 \cdot 596 \times 980 \cdot 6 = 1{,}013{,}300$ dynes per square cm.

The pressure correction when pressures are expressed in terms of barometric heights becomes

$$
\mathrm{E_{pressure}} = 0 \cdot 0000992 T \log \frac{760}{x}.
$$

Table 7 gives the magnitude of this error for a series of temperatures ranging from 10° to 40° C. corresponding to barometric readings of 760, 740 and 780 mm. taken at the respective temperatures, from which were deducted the appropriate tensions of saturated water vapour.

TABLE 7.

TYPICAL PRESSURE CORRECTIONS OF HYDROGEN ELECTRODE
POTENTIALS.

Temperature °C.		10	15	18	20	25	30	35	40
Vapour Pressure		9·2	12·8	15·5	17·5	23·8	31·8	42·2	55·3
Error volt for B.H.	(a) 760	0·0001	0·0002	0·0003	0·0003	0·0006	0·0006	0·0008	0·0010
	(b) 740	0·0004	0·0005	0·0006	0·0006	0·0008	0·0009	0·0011	0·0014
	(c) 780	−0·0002	−0·0001	−0·0001	0·0000	0·0002	0·0002	0·0004	0·0006

These figures show that for ordinary practical purposes no appreciable error is likely to be made by neglecting to make the pressure correction.

Glasstone's Modified Hydrogen Electrode.

Glasstone (*Analyst*, 1925, **50,** 327) has recently introduced a modified method for the determination of hydrogen-ion concentrations which may be of considerable use, especially in solutions containing oxidising agents that incapacitate the ordinary hydrogen electrode. It can only be applied to solutions more acid than pH 3 and more alkaline than pH 11, but may be used for solutions of intermediate pH *if those solutions are well-buffered.* We have seen that the potential of a hydrogen electrode in equilibrium with a solution containing hydrions of concentration [H·] is given at 20° C. by

$$E = 0.058 \log [H^{\cdot}].$$

If the electrode process were strictly reversible, then this potential would also be that which on passing an electric current through a solution would have to be reached before the evolution of hydrogen gas at atmospheric pressure could commence. Caspari (*Z. physikal. Chem.*, 1899, **30,** 89) found, however, that the cathodic potential at which evolution began depended upon the nature of the electrode itself. Usually, higher potentials have to be applied, and the difference between them and the calculated values are known as " overvoltage." It happens, however, that when a platinised platinum cathode is used in acid solutions the " overvoltage " is practically zero, and it is this property that Glasstone has used. Two electrodes of platinum are used, the one to serve as anode being a short piece of bright wire, and the other as cathode may be either a small piece of platinised foil or wire about 1 cm. long. These electrodes are placed in

the liquid under examination, and a gradually increasing polarising current applied from a battery of accumulators connected across a variable resistance until bubbles of hydrogen gas are just seen to be evolved at the cathode. When the potential has been adjusted such that the rate of evolution is not more than one bubble per minute, it is measured against a saturated calomel electrode. Glasstone packed the tip of the standard electrode with cotton wool to prevent the diffusion of the solution into the electrode vessel, and in order to overcome any errors due to the resistance of the solution he placed the tip of the standard electrode as close as possible to the polarised cathode during the measurement of the difference in potential between these two poles. Knowing the potential of the saturated calomel electrode, page 24, the potential of the cathode becomes known, from which the concentration of hydrogen-ions in the solution may be calculated by the usual formula.

Glasstone states that his results agreed with the author's data obtained with an exceptional hydrogen electrode, in the case of chromic acid, provided that the solution of the oxidising agent was dilute. The hydrogen-ion concentrations of solutions of nitric acid of o·1N and below agreed with those calculated from conductivity data. This polarised hydrogen electrode appeared to come to equilibrium with solutions containing large proportions of ethyl alcohol. It was inapplicable for the electrometric titration of acid by an alkali, due to the fact that the rate of removal of hydrogen-ions from the vicinity of the platinised platinum electrode was greater than their rate of replacement, with the result that the catholyte showed an enhanced pH. Identical results with those given by the hydrogen electrode were obtained for well-buffered solutions, e.g., partly neutralised acetic acid.

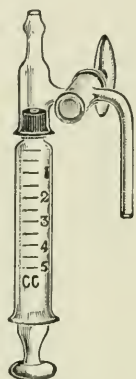## Hydrogen Electrode Vessels.

Considerably more attention has been given to the form of electrode vessel than to the more important, but more exasperating, subject of the electrode itself. Different ideas regarding the factors, which various workers believe to determine the accurate functioning of the hydrogen electrode underlie many of the vessel designs, some of which are illustrated in Fig. 6. There is probably no greater accuracy to be obtained from electrodes contained in these vessels than from the simple electrode described on page 31, provided that a satisfactory sorptive coating has been deposited upon the electrode. Two disadvantages of that form, are, however, that it is extravagant in regard to the supply of pure
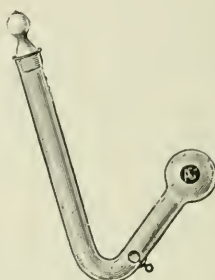
hydrogen, and that unless the ' black ' coating is satisfactory the oxygen dissolved through exposure of the solution to the air may lead to erroneous E.M.F's.   Oxygen is often present in solutions
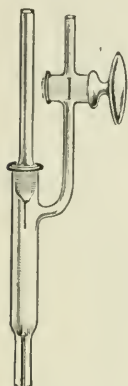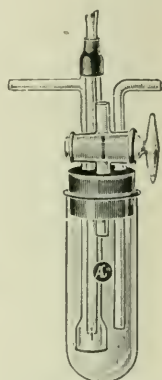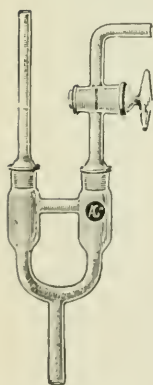

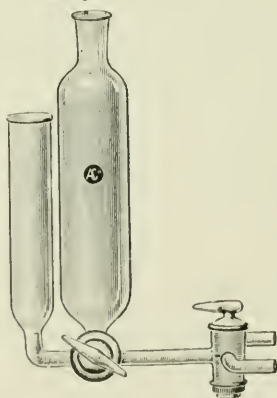Walpole.   Walpole Filler.   Bailey.   Bunker (modified).
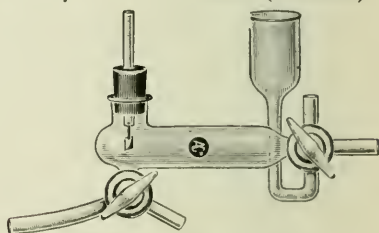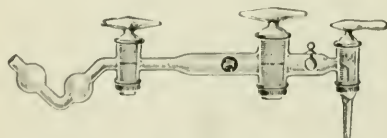
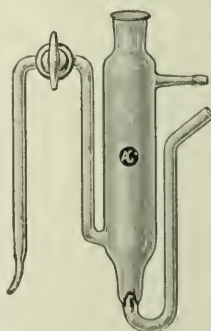Monier-Williams.   Clark Connecting Vessel.

Clark Electrode.

McClendon.   Gas Electrode.
Fig. 6.—Some Types of Hydrogen Electrode Vessels.

to be examined, especially biological fluids, *e.g.*, blood, so that this difficulty may also arise in closed vessels, and therefore will prob-ably be reduced by the electrode hydrogen.   The exclusion of

oxygen from the air may readily be effected as in the Bunker form
(*J. Biol. Chem.*, 1920, **41**, 11) which is an adaptation of the Hilde-
brand bubbling electrode. Some workers, *e.g.*, Michaelis, Wal-
pole, and Monier-Williams, saturate the platinised platinum wire
electrode with hydrogen and then allow the end to impinge upon
the surface of the solution being tested, thereby setting up a
localised equilibrium with the immediate film of liquid. Wal-
pole's vessel (*Biochem. J.*, 1913, **7**, 410 ; 1914, **8**, 131) com-
prises a tube, passing through the closed upper end of which
is a platinum wire electrode sealed into glass, fitted with a side
tube which can be used either for passing hydrogen into the elec-
trode chamber, or to suck up liquid, by means of the syringe,
through the tube at the bottom from a solution into which it dips.
The Monier-Williams vessel is similar (*The Analyst*, 1921, **46**, 315).
A platinum wire is fixed into the left-hand compartment and the
liquid sucked up into the vessel through the right-hand tube, and
then hydrogen passed into the vessel until the level of the solution
is that of the end of the electrode wire. Moloney (*J. Physical
Chem.*, 1921, **25**, 758) uses an electrode of the bubbling type, but
in order to get the electrode into equilibrium with the drop of
liquid surrounding a short wire electrode he renders a drop
sufficient to immerse the electrode, adherent by means of a loop
of glass rod placed around the wire and attached to the glass tube
into which the electrode is fixed. It should be emphasised that
in the case of electrodes which depend upon localised equilibrium
the liquid should be perfectly still whilst reading the potentio-
meter. With certain platinum black layers the oscillation of the
E.M.F. produced can be observed as each bubble of gas leaves the
vicinity of the electrode. McClendon's electrode (*J. Biol. Chem.*,
1916, **24**, 519) is a convenient form for blood work and prevents
the loss of carbon dioxide. It has a platinised gold electrode.
The Bailey electrode vessel (*J. Amer. Chem. Soc.*, 1920, **42**, 45)·
has become very popular—probably on account of its simplicity
(see Fig. 6). It contains platinised gold foil as the electrode,
and readings are taken while the electrode is completely immersed.
To use it sufficient liquid is placed in the open arm to fill it com-
pletely, so that on tilting the tube the liquid flows backwards into
the bulb and a little remains in the open arm. Hydrogen is then
led in through a narrow tube dipping into the solution. This
is allowed to raise the solution into the open arm, and after adding
more solution, if necessary, to drive out any air, the ground glass
stopper is inserted and the tube shaken vigorously for two minutes.
Afterwards the solution is allowed to cover the foil and then
connected in the usual way to a calomel electrode. Shaking

undoubtedly facilitates equilibrium, and this, together with the fact that repeated exposure of the electrode to the hydrogen gas followed by immersion in the liquid (see page 34) assists the catalytic reducing action of the hydrogen in the platinum " black " are the principles upon which the electrode vessels of Hasselbalch (*Biochem. Zeitsch.*, 1913, **49,** 451) and Clark (*J. Biol. Chem.*, 1915, **23,** 475) have been based. The Clark vessel shown in Fig. 6 is mounted on a cam, driven by a small motor, so as to give a continuous rocking motion. Hydrogen is led in at the right and connexion with the " salt bridge " is effected by opening the tap shown on the left. This is connected by means of a rubber tube to the connecting vessel shown, the larger chamber containing a saturated potassium chloride solution which can pass into the smaller vessel into which is dipped the end of a calomel electrode. (For picture of complete apparatus, see p. 109.) The gas electrode vessel given in Fig. 6 is useful in solutions not in contact with air. The usual electrode is fixed into a rubber bung and gas is passed in through the tube at the bottom, through the solution and emerges through the right-hand tube. To this tube is connected a bubbler to prevent access of air, the tube just dipping below the surface of the liquid, *e.g.*, mercury, in order that it may have no appreciable effect upon the pressure of hydrogen in the electrode vessel.

CHAPTER IV.

THE QUINHYDRONE ELECTRODE.

BIILMANN (*Ann. Chim. Phys.*, 1921, **15,** 109) was the first to show that the oxidation-reduction reaction which takes place between hydroquinone and quinone could be made use of for the measurement of hydrogen-ion concentrations, merely by dissolving some quinhydrone in the solution under investigation and observing the potential established between the solution and some unattackable metal, such as gold or platinum. We have seen on page 19 that the potential of the quinhydrone electrode,

$$E_{quin.} = \lambda + \frac{RT}{F} \log_e [H^{\cdot}],$$

when the ratio of the concentrations of hydroquinone to quinone is maintained constant.

Quinhydrone consists of fine dark bronze-green needles and is only sparingly soluble in water. It is an equimolecular compound of quinone and hydroquinone, into which it is dissociated on dissolution in water, thus

$$(C_6H_4)_2O_2(OH)_2 \rightleftharpoons (C_6H_4)O_2 + C_6H_4(OH)_2$$
Quinhydrone.   Quinone.   Hydroquinone.
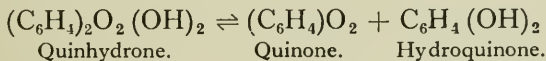
At 25° C. this dissociation proceeds to the extent of 93 per cent., and as the saturated solution is then 0·01808 M., *i.e.*, it contains 3·94 gms. quinhydrone per 100 c.c., the concentration of both hydroquinone and quinone is 0·01682 M., and that of undissociated quinhydrone is 0·00126 M.

Preparation of Quinhydrone.

Three methods are available for the preparation of quinhydrone, *viz.*: (1) combination of quinone and hydroquinone ; (2) partial oxidation of hydroquinone, and (3) partial reduction of quinone. Valeur (*Ann. Chim. Phys.*, 1900, **21** (7), 546) prepared it by the first method. He poured a solution of 20 grams of hydroquinone in 40 c.c. of 95 per cent. alcohol into a solution containing

10 grams of quinone in 300 c.c. of 95 per cent. alcohol and then set aside for 24 hours. The precipitated crystals were washed with a little alcohol and dried between filter papers, the last traces of alcohol being removed by standing over sulphuric acid in a desiccator. Yield 17·5 grams. When heated rapidly in a capillary tube the melting-point is found to be 172° C.

Biilmann (*Trans. Faraday Soc.*, 1923, **19,** 57) prepares it by the second method by dissolving 100 grams of iron alum, *i.e.*, ferric ammonium sulphate, in 300 c.c. of water at 65° C., pouring into a solution of 25 grams of hydroquinone in 300 c.c. of water, cooling in ice and separating the crystals by suction. In this way a yield of 15 grams may be obtained, and after washing four or five times with water, the quinhydrone should contain only a trace of iron, which, according to Biilmann, does not affect the E.M.F. of the electrode.

After drying the quinhydrone between filter papers in air for a couple of days, it should be placed in a well-stoppered bottle to prevent any possible oxidation. If drying by heat is resorted to there is a risk if the temperature becomes too high of some of the more volatile component, quinone, vaporising, though the amount which occurs, if any, when it is dried for the minimum time in an ordinary steam-oven has been found to be without effect on the E.M.F. when tested in buffer solutions of known pH.

The platinum electrodes should be highly polished and clean. Cleaning should be carried out by treatment with a hot mixture of chromic acid and concentrated sulphuric acid, washed with distilled water and heated to a red heat in an alcohol steam lamp or in a benzine blow lamp, but not in a gas flame.

Use of Quinhydrone Electrode : Advantages and Disadvantages.

In order to determine the concentrations of hydrogen-ions with quinhydrone all that is necessary is to dissolve a little in the solution, place in it a piece of bright platinum or gold to serve as one pole of the cell and then connect up the solution through a saturated potassium chloride solution bridge to some standard electrode and measure the potential difference between the two electrodes. The potential at the surface of the noble metal electrode is produced almost momentarily. It is stated, however, that this is not so when an electrode has been immersed in one solution and then transferred to another solution of considerably different pH, a much longer time often being necessary if a small error is to be avoided. There is sometimes a tendency for the

E.M.F's to lag behind when the electrode is being used for titra-
tion work and the hydrogen-ion concentration is undergoing a
sharp change.   As Biilmann and Jensen (*Bull. Soc. Chim.*, 1927,
41 (4), 151) have shown, the solution need not be saturated with
respect to quinhydrone to give reproducible potentials, and they
found by using one-tenth of the amount required for saturation,
viz., 0·35 gram per 100 c.c., the error was within a millivolt at
18° C.   It is advisable to have sufficient quinhydrone to make
the solution 0·005 M. (1·1 gm. per 100 c.c.).   It is immaterial
whether the solution in the electrode vessel has access to the air.
The area of the unattackable electrode should be as large as pos-
sible, since the larger it is the larger the current that can be drawn
from the cell without appreciably disturbing the equilibrium
when determining the null point on the potentiometer.   The
platinum electrode is fused on to platinum wire which is fused
into the closed end of a glass tube containing mercury to pro-
vide a contact for copper wire.   Care must be taken to ensure
perfect sealing-in of the platinum wire, or mercury may very slowly
leak through and make contact with the solution.   This may affect
the potential by many millivolts.   Where the hole is extremely
minute it is sometimes a difficult matter to detect such a defect.

By comparison of the potentials of the quinhydrone electrode
in solutions of definite pH with those set up by the hydrogen
electrode, the potential of each electrode being measured against
the same standard half-element, it is found that those of the quin-
hydrone electrode at 18° C. are more positive than those of the
hydrogen electrode by 0·7044 volt.   This will be seen from
Table 4 in which the voltages are given for both the hydro-
gen and quinhydrone electrodes when compared with that of
the normal calomel electrode.   Hence it follows that when [H˙]
becomes equal to 1 molar in the expression given above the last
term, *viz.*, $\dfrac{RT}{F} \log_e$ [H˙] becomes zero, and then

$$E_{quin.} = \lambda = 0 \cdot 7044 \text{ volt.}$$

Hence, *provided the ratio of quinone to hydroquinone in the solution
remains equimolecular*,

$$E_{quin.} = + 0 \cdot 7044 + 0 \cdot 0001984T \log [H˙]$$

at a temperature T° Absolute.

As mentioned before, the value 0·7044 volt is the reduction
potential of quinone in a solution containing 1 gram-mol. of
hydrogen ions.   It varies with temperature and has a fairly large
negative temperature coefficient.   The precise value for any

temperature between $0°$ and $37°$ C. can be calculated from the formula

$$\epsilon_t = 0.7175 - 0.00074t \text{ volt},$$

where ϵ_t is the voltage at $0°$ C. and t is temperature in degrees Centigrade. Thus, at $18°$ to $20°$ C.

$$E_{quin.} = 0.704 + 0.058 \log [\text{H}^{\cdot}].$$

Compared with the potentials of the standard calomel electrodes the potential of the quinhydrone electrode in acid solutions is positive, but becomes equal to, and subsequently negative to the calomel standards when the hydrion concentrations fall below definite pH's. This may be seen from the last column of Table 4 where the potentials against the calomel electrodes become smaller with increasing pH, becomes equal to that of the normal calomel electrode at a pH value between 7 and 8, and thereafter becomes negative. This will also be seen to be true when the electrode is used in conjunction with the saturated calomel electrode from the electrometric titration data of La Mer and Parsons (*J. Biol. Chem.*, 1923, **57**, 622) given in Table 8.

TABLE 8.

ELECTROMETRIC TITRATIONS AT $25°$ C. OF 20 C.C. 0.200 M. ACETIC ACID WITH 0.204 N—NaOH.

c.c. NaOH.	E.M.F. against Saturated Calomel of		pH (Hyd. El.).	pH (Quin. El.).	E.M.F. Quin. E. −Hyd. El	pH Error of Quin. El.
	Hydrogen E.	Quinhydrone E.				
0.00	− 0.406	+ 0.294	2.86	2.68	0.700	− 0.18
2.00	− 0.466	+ 0.233	3.71	3.71	0.699	0.00
4.00	− 0.486	+ 0.214	4.05	4.04	0.700	− 0.01
6.00	− 0.499	+ 0.201	4.27	4.26	0.700	− 0.01
8.00	− 0.510	+ 0.189	4.45	4.45	0.699	0.00
10.00	− 0.520	+ 0.179	4.63	4.62	0.699	0.00
12.00	− 0.531	+ 0.168	4.80	4.80	0.699	0.00
14.00	− 0.543	+ 0.156	5.02	5.02	0.699	0 00
16.00	− 0.558	+ 0.140	5.26	5.26	0.699	0.00
17.00	− 0.569	+ 0.130	5.45	5.45	0.699	0.00
18.00	− 0.582	+ 0.114	5.70	5.72	0.696	+ 0.02
18.50	− 0.595	+ 0.103	5.89	5.90	0.698	+ 0.01
19.00	− 0.616	+ 0.084	6.25	6.22	0.701	− 0.03
19.40	− 0.670	+ 0.044	7.16	6.91	0.714	− 0.25
19.50	− 0.737	+ 0.029	8.30	7.16	0.766	− 1.24
19.80	− 0.892	− 0.048	10.90	8.47	0.844	− 2.43
20.00	− 0.909	− 0.071	11.20	8.85	0.838	− 2.35
20.50	− 0.925	− 0.102	11.50	9.36	0.803	− 2.14
21.00	− 0.934	− 0.119	11.63	9.66	0.815	− 1.97
21.50	− 0.940	− 0.132	11.71	9.86	0.808	− 1.85
22.00	− 0.945	− 0.145	11.85	10.10	0.800	− 1.75
22.50	− 0.948	− 0.156	11.88	10.29	0.792	− 1 59

The measured potential difference between a quinhydrone and a standard calomel electrode is given by

$$\text{E.M.F.}_{(observed)} = E_{quin.} - E_{standard}$$
$$= 0.704 + 0.058 \log [H^{\cdot}] - E_{standard}$$

and, therefore, at $18°$ to $20°$ C.,

$$p\text{H} = \frac{0.704 - E_{standard} - E_{observed}}{0.058}.$$

If the standard electrode is Veibel's quinhydrone electrode, p. 29, then at $18°$ C. the above expression reduces to the following :—

$$p\text{H} = -2.04 + \frac{E_{observed}}{0.0577}.$$

The chief advantages of the quinhydrone electrode are that

(*a*) it attains equilibrium rapidly ;
(*b*) it may often be used in solutions containing oxidising agents and salts of metals more noble than hydrogen, for which the hydrogen electrode is inapplicable ;
(*c*) it is not so readily incapacitated as the hydrogen electrode.

Its disadvantages are that

(*a*) it cannot be used in solutions of $p\text{H} > 8$;
(*b*) there is a possibility of side reactions taking place which may alter the molecular ratio of quinone to quinhydrone ;
(*c*) it has appreciable " protein-errors " ;
(*d*) it has " salt-errors," though often extremely small.

Although the quinhydrone electrode is limited chiefly to the acid side of neutrality, the fact that it can give steady and reproducible potentials in the presence of oxidising agents opens up a field of usefulness not covered by the hydrogen electrode. Needless to say, the experimenter must always be on the look out for unsteady E.M.F's through side reactions taking place which may materially affect the constancy of the 1 : 1 ratio. Except for the great convenience in using the compound, quinhydrone, there is no reason why other ratios of quinone to hydroquinone might not be used, and, indeed, both the hydro-quinhydrone and the quino-quinhydrone electrodes have been used, in the former electrode the solution was saturated with both hydroquinone and quinhydrone, and in the latter, with quinone and quinhydrone.

Alteration of the ratios merely introduces another term of constant value into the expression connecting the E.M.F. with hydrogen-ion concentration. Thus at 18° to 20° C., the potentials of these electrodes may be expressed by the following formulæ :—

$$E_{\text{hydro-quinhydrone}} = 0 \cdot 618 + 0 \cdot 058 \log [\text{H}^{\cdot}]$$
$$E_{\text{quino-quinhydrone}} = 0 \cdot 756 + 0 \cdot 058 \log [\text{H}^{\cdot}].$$

These electrodes have no advantages over the ordinary quin-hydrone electrode. Side-reactions are probable only with strong oxidising and reducing agents such as ferric and titanous salts, and also with more concentrated solutions of nitric and chromic acids.

In addition to those solutions in which the hydrogen electrode can be used, the quinhydrone electrode can be used in solutions of copper salts, unsaturated acids, dilute nitric acid, and nitrates and alkaloids. It may also be safely used in many biological and natural solutions where the hydrogen electrode would cause reduction. Biilmann has shown that it may be used in presence of nitric, acrylic, crotonic, fumaric, maleic, and phenylpropiolic acids.

Strictly speaking the reason for this increased applicability of the quinhydrone electrode over that of the hydrogen electrode is to be found in the magnitude of the reduction potential of quinone ; but Biilmann, by means of calculations similar to those carried out on page 48 for hydrogen electrodes at different pressures of hydrogen gas, has shown that, in effect, the quinhydrone elec-trode might be considered as a hydrogen electrode having an extremely small pressure of hydrogen gas and consequently possessing very small reducing action. Though the figures so obtained can have no real physical meaning, they may perhaps lead to a better appreciation of the cause of the utility of the quin-hydrone electrode.

If the reaction between quinone and hydroquinone be regarded in a purely chemical sense, then it may be represented thus

$$\text{H}_2 + \text{C}_6\text{H}_4\text{O}_2 \rightleftharpoons \text{C}_6\text{H}_4\text{O}_2\text{H}_2$$
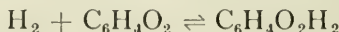
whence by the law of mass action

$$[\text{H}_2] = \text{K} \cdot \frac{[\text{hydroquinone}]}{[\text{quinone}]}$$

or,

$$\pi = \text{K}' \cdot \frac{[\text{hydroquinone}]}{[\text{quinone}]}$$

where π is regarded as the hypothetical pressure of hydrogen gas. Now we have seen that the E.M.F. of a cell composed of two hydrogen electrodes at different hydrogen pressures is given by

$$E_{pressure} = 0 \cdot 0000992 \log \frac{1}{\pi},$$

and as the potential of the quinhydrone electrode is 0·704 volt above that of the normal hydrogen electrode, we see that the E.M.F. of cell constituted of these two electrodes in the same solution will be

$$0 \cdot 704, \text{ or } E_{pressure} = 0 \cdot 704.$$

In this way Biilmann has calculated that at 18° C. the quinhydrone corresponds to a hydrogen electrode having a hydrogen pressure of $10^{-24\cdot4}$ atmospheres, at $10^{-23\cdot6}$ atmospheres at 25° C. Such fictitious pressures can have no real significance, though as Biilmann points out they may " serve " as very useful characteristics of the reducing powers of the electrode substances. A pressure of $10^{-24\cdot4}$ atmospheres corresponds to 1 molecule of gas in about 90 litres, so that in the amount of a solution undergoing examination there would not be one single molecule of hydrogen.

The great drawback to the quinhydrone electrode is that it cannot be used in solutions of above pH 8. This is because hydroquinone behaves as a dibasic acid and then begins to have an effect upon the hydrogen-ion concentration of the solution. In the case of a solution containing no buffers (see later) this effect may be great at the comparatively low pH values, though with a buffered solution the error thereby introduced may not become considerable until considerably higher pH values are reached. Sheppard (*Trans. Amer. Electrochem. Soc.*, 1921, **39**, 429) found that K_1 of hydroquinone is $1 \cdot 75 \times 10^{-10}$, *i.e.*, $pK_1 = 9 \cdot 8$; and the second dissociation constant, K_2 to be 4×10^{-12}, $pK_2 = 11 \cdot 4$. Generally the concentration of hydroquinone is about 0·01 M., and consequently, if pure water were being examined we should be concerned with the hydrogen-ions produced by the dissociation of the water,

$$H_2O \rightleftharpoons H^{\cdot} + OH'$$

and those liberated by the first stage of dissociation of hydroquinone, H_2Q,

$$H_2Q \rightleftharpoons H^{\cdot} + HQ'.$$

By the principle of the electro-neutrality of solutions, we find that

$$[H^{\cdot}] = [OH'] + [HQ']$$

the concentration of ions arising from the second stage of dissociation here being considered negligible. As

$$K_w = [H^{\cdot}][OH'] \text{ and } K_1 = \frac{[H^{\cdot}][HQ']}{[H_2Q]}$$

we get

$$[H^{\cdot}]^2 = K_w + K_1 [H_2Q].$$

Very often K_w is negligible compared with the other term, i.e., when K_1 is fairly great. In the case of hydroquinone its effect is scarcely perceptible. It is found from this expression that pure water, pH 7·0, when tested with the quinhydrone electrode would show a pH of 5·9 with a concentration of 0·01 M.-hydroquinone, and pH 6·4 with a 0·001 M.-solution. Appreciable errors may thus be obtained in unbuffered solutions whose pH values are about 6. If the solution contains buffering agents then no great error might be expected to occur until about pH 8, for as will be shown later only 1 per cent. of neutralisation of the first stage of hydroquinone can occur before pH 9·8 − 2·0 = pH 7·8.

This functioning of hydroquinone as an acid leads to another error, that of disturbing the molecular ratio of quinone to hydroquinone for the concentration of undissociated hydroquinone becomes reduced. Biilmann calculates that at pH 8, the ratio becomes 1·01 : 1, voltage error = 0·0001 volt ; at pH 9, the ratio is 1·10 : 1 with a resulting error of 0·001 volt.

The last column of Table 8 shows that the pH values calculated from the data given by the quinhydrone electrode began

TABLE 9.

COMPARATIVE pH VALUES OBTAINED BY KOLTHOFF ON BUFFER SOLUTIONS.

Buffer Solution.	pH Hydrogen Electrode.	pH Quinhydrone Electrode.	Error of Quinhydrone Electrode.
0·05 M. KH$_2$PO$_4$ and 0·05 M. borax mixtures	6·20 6·27 7·04 8·30	6·17 6·27 7·00 8·33	− 0·03 0·00 − 0·04 + 0·03
KH$_2$PO$_4$—NaOH mixtures. Clark	7·20 7·60	7·25 7·62	+ 0·05 + 0·02
Boric—NaOH mixtures. Clark	8·20 8·80 9·20 9·60	8·20 8·80 9·24 9·49	0·00 0·00 + 0·04 − 0·11

to be erroneous at pH 6. This corresponded to the final part of neutralisation of acetic acid when the buffering capacity had almost disappeared. When the solutions contain buffers then the quinhydrone electrode potentials may be expected fairly accurate pH values up to about 9. This will be seen from the values of Kolthoff (*Z. physiol. Chem.*, 1925, **144**, 259) given in Table 9.

Colloidal material, and especially certain proteins give rise to errors, though Linderstrøm-Lang (*Comp. rend. Lab. Carlsberg*, 1925, **16** (3), 1), by comparison with the pH values calculated from hydrogen electrode potentials, has found that it is possible to apply suitable corrections to the quinhydrone pH values. Such corrections are, however, not always possible. The extent of these errors is indicated in Table 10 :—

TABLE 10.

COMPARATIVE pH VALUES OBTAINED BY KOLTHOFF ON PROTEIN SOLUTIONS.

Solution.	pH Hydrogen Electrode.	pH Quinhydrone Electrode.	Error of Quinhydrone Electrode.
Blood serum with NaCl	6·04 6·06	5·94 5·88	− 0·10 − 0·18
Blood serum with NaCl and Na$_2$HPO$_4$	6·85 7·04 7·18	6·71 6·89 7·00	− 0·14 − 0·15 − 0·18
Casein—NaOH solution	6·59 7·03 7·19 7·42 7·69	6·51 6·94 7·10 7·29 7·45	− 0·08 − 0·09 − 0·09 − 0·13 − 0·24

The potential of the quinhydrone electrode may be slightly affected by the concentrations of neutral salts—the errors are generally negligible. Sørensen has shown that when the total concentration of salt is 0·2 M. the error is about 0·01 pH, and in the case of a decinormal hydrochloric acid solution which was 4-normal with respect to NaCl the error had only become 0·2 pH.

It should be borne in mind that the behaviour of the quinhydrone electrode is always standardised against that of the hydrogen electrode, and that all the foregoing errors correspond with divergences from it produced by the quinhydrone electrode. These electrodes should from time to time be tested in buffer solutions of known pH. In acid solutions the quinhydrone

electrode gives almost immediately steady voltages which remain constant over prolonged periods. In alkaline solutions oxidation of the hydroquinone occurs more readily as shown by a darkening in the colour of the solution. Its rate increases with increasing pH, though it is reduced somewhat in well-buffered solutions. Much of this oxidation is caused by the action of air, and it may be diminished and sometimes eliminated by using an enclosed electrode vessel and passing through it some inert gas, e.g. nitrogen. For fuller information regarding the use of the electrode for titration purposes the reader is referred to a paper by Rabino-witsch and Kargin (Z. *Elektrochemie*, 1927, **33**, 11).

Continuous Recording of pH values with Quinhydrone Electrode.

The fact that very small currents may be drawn from a cell incorporating a quinhydrone electrode without materially disturbing the equilibrium makes it possible to employ it for making
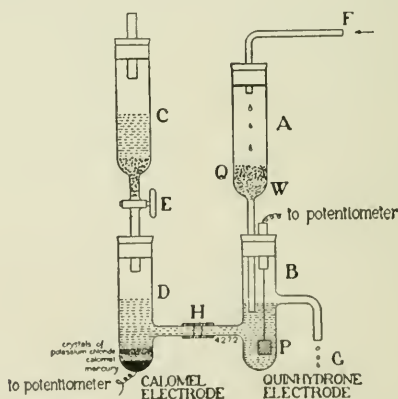

FIG. 7.—Recording Quinhydrone Electrode (Cambridge Instrument Co., Ltd.).

a continuous record of the fluctuations of the concentrations of hydrogen-ions of a solution. Such an electrode has been used in the sugar industry and in nickel plating. This advantage is not shared by the hydrogen electrode, and in the potentiometric measurements every care must be taken not to extract any current from the cell. Thus the Cambridge Instrument Co. state that a current to the extent of 5 micro-ampères may be taken from a quinhydrone-calomel cell without disturbing its potential difference to an appreciable extent. This extremely small current is sufficient to work their standard thread automatic recording volt-

meter, designed originally for pyrometer work, and thereby to give a continuous record of variations in hydrogen-ion concentration with a fair accuracy.

Fig. 7 is a diagram of the apparatus with which their experiments were carried out in which the solution after being cooled to a maximum temperature of 30° C., passes through the inlet tube F into the vessel A which contains crystals of quinhydrone Q resting on a wad of glass wool W. The solution, saturated with quinhydrone, then enters the lower vessel B, containing a gold or platinum electrode P, finally overflowing through G. A bridge is thus formed through H with the saturated calomel half-cell D and the E.M.F. is measured on either their potentiometer or recording thread voltmeter. (See also Parker, *J. Ind. Eng. Chem.*, 1927, **19,** 660 ; Parker and Greer, *Trans. Amer. Electrochem. Soc.*, 1926, **49.**)
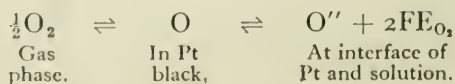
CHAPTER V.

THE OXYGEN AND AIR ELECTRODES.

THE oxygen and air electrodes, like that of hydrogen depends upon the absorption of gas by platinum black, and, as an instrument of control in technical processes, the Hildebrand type of gas electrode described on page 31 is quite satisfactory, witų the exception that either oxygen or simply air is passed through instead of hydrogen.

Although the oxygen electrode (or air electrode) is, in general, readily responsive to the changes in hydrogen-ion concentration, and may be used for the purification by graded precipitation from solutions, such as those of copper sulphate containing ferric salts (for which the hydrogen electrode is unsuited), by treatment with alkalis (*vide* Tilley and Ralston, *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 79 ; Britton, *J. Chem. Soc.*, 1925, **127**, 2148), and of boiler-feed water (Arthur and Keeler, *Power*, 1922, **55**, 768), the fact that it is irreversible does not allow of the direct calculation of the hydrogen-ion concentrations. The E.M.F's which it registers over known ranges of pH can, however, be calibrated with a fair degree of accuracy in terms of pH or hydrogen-ion concentration (cf. Britton, *loc. cit.*, 1924, **125**, 1574). The cause of its irreversibility lies in the tendency of the gas to combine with the platinum to form a series of oxides or perhaps of " solid solutions."

The theory of the oxygen electrode rests on the fact that to a large extent, though not completely, the oxygen electrode enters into equilibrium with the hydroxyl-ions, and, consequently, the hydrogen-ions, thus $O'' + H_2O \rightleftharpoons 2OH'$. If the reactions which prevail at the platinum black surfaces could be correctly expressed by the following scheme,

$$\tfrac{1}{2}O_2 \quad \rightleftharpoons \quad O \quad \rightleftharpoons \quad O'' + 2FE_{O_2}$$

| Gas phase. | In Pt black, | At interface of Pt and solution. |

then we see from page 12 that the potential between the electrode and the solution could be expressed by the following equations :—

$$E_{O_2} = \frac{RT}{2F} \log_e \frac{P}{p} = \frac{RT}{2F} \log_e \frac{C}{c}$$

$$= \epsilon_{O_2} - \frac{0.058}{2} \log [O'']$$

at 18° to 20° C.

The normal electrode potential of oxygen is $+ 0.41$ volt, and therefore it might be expected that

$$E_{O_2} = 0.41 - \frac{0.058}{2} \log [O'']$$

and as an equilibrium must be set up between the oxygen-ions and hydroxyl-ions,

$$O'' + H_2O \rightleftharpoons 2OH'$$

$$\therefore \frac{[OH']^2}{[O'']} = K,$$
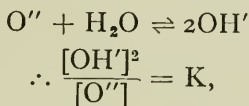
whence $\quad E_{O_2} = 0.41 - \frac{0.058}{2} \log \frac{[OH']^2}{K}$

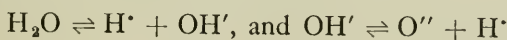$$= 0.41 + 0.029 \log K - 0.058 \log [OH'].$$

But the equilibrium between the hydroxyl-ions and the hydrogen-ions is given by

$$[H^·][OH'] = K_w,$$

whence by substitution, we find that if the oxygen electrode were reversible,

$$E_{O_2} = 0.41 + 0.029 \log K - 0.058 \log K_w + 0.058 \log [H^·]$$
$$E_{O_2} = \lambda + 0.058 \log [H^·]$$
$$= \lambda - 0.058 \, p\text{H}.$$

This expression might also have been obtained from a consideration of a series of equilibria as follows :—

$$H_2O \rightleftharpoons H^· + OH', \text{ and } OH' \rightleftharpoons O'' + H^·$$

and $\quad\quad\quad \therefore [O''] = \frac{K_w \cdot k}{[H^·]}.$

The E.M.F. of a hydrogen electrode immersed in the same solution as an oxygen electrode would be

$$E_{H_2} = 0.058 \log [H^·],$$

and consequently the potential difference between the oxygen and hydrogen electrodes constituting such a cell would be equal to

$$\text{E.M.F.} = E_{O_2} - E_{H_2} = \lambda \text{ volts,}$$

the oxygen electrode being positive.

In a similar manner, if we consider the E.M.F. of cell composed of a hydrogen electrode immersed in a solution of concentration $[H^{\cdot}]$ and a standard electrode, say, the normal calomel electrode, and also the E.M.F. of a combination of an oxygen electrode in a solution of the same concentration of hydrions and a normal calomel, then we find that E.M.F. of $O_2 \mid - \mid$ N-calomel

$$- \text{E.M.F. of } H_2 \mid - \mid \text{N-calomel}$$
$$= \lambda \text{ volt.}$$

It follows, that if the oxygen electrode behaved in a reversible manner we should expect it to indicate potentials which were always more positive by a constant value, λ, the theoretical potential of the oxygen-hydrogen cell, or the so-called *Knall-Gas Kette*, than that of a hydrogen electrode in the same solution. This quantity will be referred to later in connexion with efforts which have been made to study both the behaviour of the oxygen electrode and possible methods for calibrating its potentials for the purpose of calculating hydrogen-ion concentrations.

Nernst and Wartenberg (*Z. physikal. Chem.*, 1906, **56,** 534) found, by extrapolation from the results obtained in their classical researches on the dissociation of steam at high temperatures, that the potential difference of the oxygen-hydrogen cell at the ordinary temperature could be calculated from the expression E.M.F. $= 1 \cdot 232 - 0 \cdot 00085 \, (t^\circ - 17)$, and therefore the E.M.F. at 20° should be $1 \cdot 229$ volts. Similar values have been obtained by indirect methods based on the potential of $Ag \mid Ag_2O \cdot NaOH$ electrode and the dissociation pressure of silver oxide (*vide* Britton, *J. Chem. Soc.*, 1925, **127,** 2960). Thus, if the oxygen in the platinum black, or even in the bare surface of bright platinum, behaved in a strictly reversible way as is the case with hydrogen we should expect the potentials of the oxygen electrode to be $1 \cdot 229$ volts more positive than those of a hydrogen electrode when immersed in the same solutions at 20° C. Actual measurements of the E.M.F. of an oxygen-hydrogen cell show that true equilibrium values appear to be never attained, but give final values which lie between $1 \cdot 08$ and $1 \cdot 14$ volt. Hence, it was thought that, even if the difference between the voltage of the oxygen electrode and the hydrogen electrode did not become equal to $1 \cdot 229$ volt, it might at least

acquire some definite and characteristic value and thereby would permit of the calibration of each individual oxygen electrode for the determination of pH values. Provided that the oxygen electrode is subjected to no sudden variations in hydrogen-ion concentration then it may be reasonably expected that its voltages will be parallel to those of a hydrogen electrode in equilibrium with the same solution. This is usually true, but if the solution contains either oxidising or reducing agents it will be found that they often exert some influence on the electromotive force such that its relationship with the hydrogen electrode becomes altered, for then the concentration of oxygen-ions will be dependent both upon the concentration of hydrogen-ions and that of the oxidising or reducing agents. The effects of these agents become more pronounced within certain ranges of pH. Although the oxygen electrode when placed in a solution does not actually attain a constant E.M.F., it is found that in general a value is shown after oxygen has been passed for about 15 minutes which varies only slightly with time—a matter of a few millivolts. As was first pointed out by Furman (*J. Amer. Chem. Soc.*, 1922, **44**, 12) this does not detract from its use in electrometric titrations for the variations in potential due to variations in hydrogen-ion concentration overpower the " drift " due to the oxygen electrode itself. He has shown its use for the accurate electrometric titrations of acids and alkalis in solutions of coloured oxidising agents, *e.g.*, potassium chromate, potassium permanganate, and potassium ferricyanide, in whose presence the hydrogen electrode would, of course, be useless, and whose colour may prevent titration with the usual indicators. Bright platinum-oxygen and air electrodes have been used for the determination of the " acid number " of acids and fats with alcoholic potassium hydroxide (Kremann and Schöpfer, *Die Seife*, 1922, **8**, 35), and for the titration of alkaloids, quinine, cocaine, cinchonidine and strychnine, by Popoff and McHenry (*J. Amer. Pharm. Assoc.*, 1925, **14**, 473). The oxygen electrode has been employed for the control of the hydrogen-ion concentration of boiler feed-water, which through the dissolved oxygen would make the hydrogen electrode unsuited, especially as the solutions were allowed to flow through the electrode chamber. Thus Arthur and Keeler (*loc. cit.*) used it in connexion with the purification of boiler feed-water in conjunction with a decinormal calomel electrode, and, moreover, found that the dissolved oxygen was sufficient to maintain the electrode in a saturated state. They were able to obtain by means of an automatic recording potentiometer, a satisfactory record of the reaction of the water, and by a system of relays and contacts they found

that a motor-operated valve could be made to control automatically the additions of alkali when necessary.

It is probable that the oxygen electrode is applicable to most of the solutions in which the hydrogen electrode is useless, though the author has found that in sulphite solutions both electrodes fail.

Air, free from carbon dioxide, may be used to saturate the platinum with oxygen (*vide* Furman, *Trans. Amer. Electrochem. Soc.*, 1923, **43**, 79), which from theory it would be expected to produce an electrode 0·008 volt less positive than the oxygen
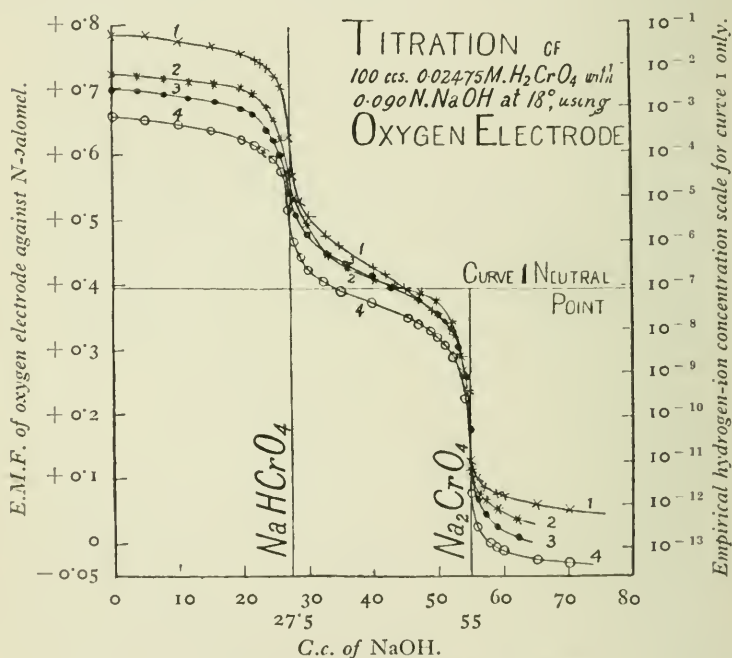

Fig. 8.—Oxygen Electrode Titration Curves.

electrode under atmospheric pressure. Actually, such a difference is often masked by the anomalous behaviour of the oxygen in the electrode.

It may be an advantage to summarise here some of the author's observations regarding the oxygen electrode (*J. Chem. Soc.*, 1924, **125**, 1572 ; 1925, **127**, 1896, 2148, 2964). Figs. 8 and 9 refer to the oxygen electrode tirations of chromic, malonic, tartaric and oxalic acids with approximately decinormal sodium hydroxide, the comparison electrode being the normal calomel. Each of these titrations were also performed with the hydrogen electrode

(see pages 145, 149) and therefore the E.M.F's of the oxygen-hydrogen cell could be extrapolated from the curves given by the two different electrodes. It might be thought that any particular oxygen electrode when placed in the same solution on different occasions would assume or at any rate tend to approach the same potential, so that once an electrode had been standardised against a hydrogen electrode some approximate idea of the hydrogen-ion concentration of a solution could be calculated from its E.M.F.
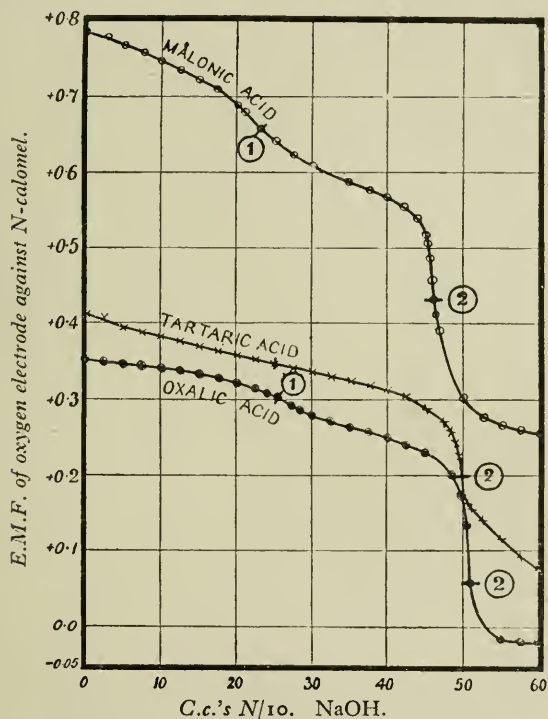

FIG. 9.—Oxygen Electrode Titration Curves.

set up in another solution at some subsequent time. This, however, is not the case, for the difference between the oxygen and hydrogen electrode potentials vary appreciably on keeping, even though the electrodes are kept between use immersed in distilled water. Thus in Fig. 8 curves 1 and 2 were given simultaneously by two different electrodes in the same solution on one day, but on the next day the curves obtained with the respective electrodes were 4 and 3. The curves given in Fig. 9 were obtained with the same electrodes on three successive days, that of malonic acid
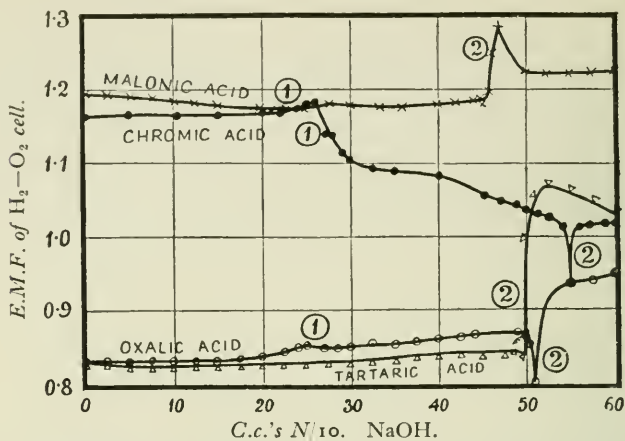
FIG. 10.—Comparison of Oxygen Electrode and Hydrogen Electrode Titration Curves on the Basis of the Oxygen-Hydrogen Cell.
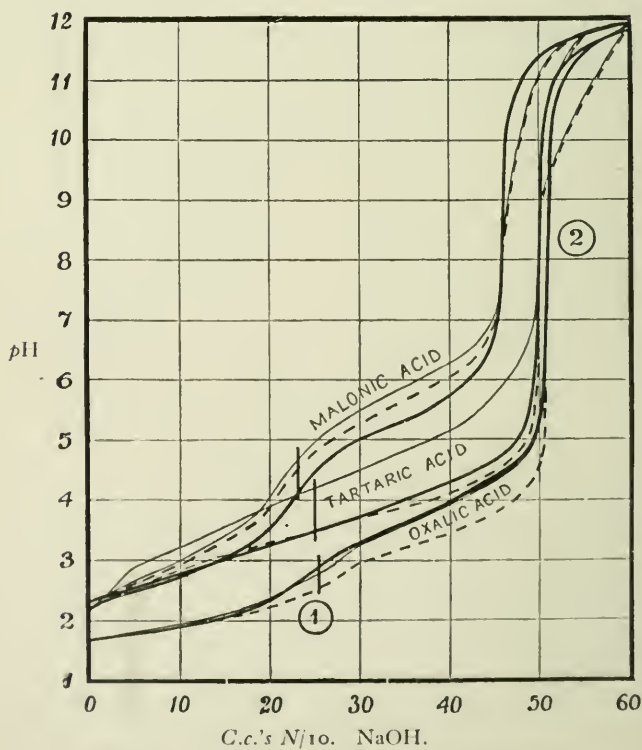

FIG. 11.—Adjusted Oxygen Electrode Curves.

on the first, tartaric acid on the second, and oxalic acid on the last.
It is surprising that the initial voltages were so different seeing that
the pH values of the malonic and tartaric acids were pH 2·28 and
pH 2·29 respectively, while that of oxalic acid was pH 1·65, and
consequently it might have been expected that the potential of the
oxygen electrode in the oxalic acid would have been considerably
more positive.   These curves show, then, that the oxygen elec-
trodes on ageing lose much of their value as indicator electrodes.
Though they are capable of indicating end-points, the sudden
falls in potential differences which occur in the vicinity of these
points become less in extent, and thereby render it more difficult
to locate the point of inflexion at the true end-point with accuracy.

It was stated above that oxidising agents affect the potentials
of the oxygen electrode, and also that there was a lag in the poten-
tials of the oxygen electrode when it was being subjected to a
rapid change in hydrogen-ion concentration.   This will be seen
from Fig. 10 in which the extrapolated E.M.F's of the oxygen-
hydrogen cell corresponding to the different stages of the titration
of the four acids are given.   The curves show that the variations
in the extrapolated E.M.F's at the beginnings and endings of the
different titrations, given in Table 11, were not incorporated

TABLE 11.

Acid.					E.M.F. of Oxygen-Hydrogen Cell at		
					Beginning.	End.	Difference.
Malonic	.	.	.	.	.	1·195	1·228	+ 0·033
Tartaric	.	.	.	.	.	0·828	1·034	+ 0·206
Oxalic	.	.	.	.	.	0·830	0·950	+ 0·120
Chromic	.	.	.	.	.	1·162	1·027	− 0·135

proportionally in the oxygen electrode voltages throughout the
whole courses of the titrations, but were chiefly introduced in the
final stages of the neutralisations.   It was thought that these
differences were due simply to a lag in the E.M.F's of the oxygen
electrodes caused by the considerable change in hydrion concen-
tration, which could be overcome by allowing time before taking
further readings.   When the change was considerable, it was
sometimes found that time produced some little effect, but in
general, the extrapolated E.M.F's never fell to the initial values.
This change which takes place as the titrated solution attains
alkalinity seems to be connected both with the age of the electrodes

and with the oxidising nature of the acids. The curve showing
the change which took place in the titration of chromic acid is
given in Fig. 10, the actual titration curve being No. 1 in Fig. 8.
Although there was no change in the P.D. during the first half of
the neutralisation, there was a somewhat irregular falling off dur-
ing the second stage, and when the solution had become alkaline
it was found that the extrapolated E.M.F. was less than the initial
value. This occurred in every one of the many titrations under-
taken. The hydrogen-ion concentration prevailing during the
second half of the titration lay between 10^{-6} and 10^{-7}, and it
seems that it was here and later in the alkaline solution that the
oxidising nature of the chromic acid came into play. No irreg-
ularities occurred with the non-oxidising acids and especially
with malonic acid, the second part of the neutralisation of which
was not far removed from the neutral point.

Calibration of the Oxygen Electrode in Titrations.

The erratic behaviour of the oxygen electrode whilst being
subjected to rapid changes in hydrion concentration, such as
shown (Fig. 9) to take place at the end-points of titrations, renders
it almost impossible to affix a satisfactory hydrogen-ion concen-
tration scale to the measured voltages. It is possible, however,
to get an approximate idea of the changes in pH over the greater
range of the titration, for which purpose the following two schemes
of calibration have been examined.

First, knowing the pH's of solutions at two remote stages of
a titration and the corresponding voltages given by the oxygen
electrode, one assumes that the intermediate pH's are proportional
to the observed E.M.F.'s. Such a scale is affixed to one of the
chromic acid curves, Fig. 8, and permits of pH values being
read off accurately to within 0·5 pH unit, except from that portion
of the curve around the end-point. In Fig. 11 hydrogen elec-
trode titration curves (heavy lines) of the three organic acid
solutions which were studied with the oxygen electrode together
with the approximate pH curves calibrated from the oxygen
electrode data. The thin unbroken lines referring to pH values
were arrived at on the basis suggested above. Except in the case
of the oxalic acid curve the agreement with hydrogen electrode
curves is unsatisfactory—the great errors indicated by the tartaric
acid being due to a lag of 0·206 volt introduced at the end-point
being divided proportionally over the whole range of voltages
covered by the titration. Hence it appears that when the extra-
polated E.M.F.'s of the oxygen-hydrogen cell for the initial and

final stages of an oxygen electrode titration are widely different, a simple proportional pH scale may be very far from satisfactory.

The second method of calibration was based on the fact, illustrated by Fig. 10, that the oxygen electrode voltages are more positive than the corresponding hydrogen electrode voltages by approximately a fixed amount when working over a range of hydrion concentration which does not involve sudden changes, and that the appreciable variations occur only when a very sharp change in hydrion is encountered.   Thus in any one of the present titrations, if the pH's at the beginning and at the end are known, the E.M.F.'s given by the hydrogen electrode as compared with the normal calomel can be calculated, and thus the P.D. of the corresponding oxygen-hydrogen cells can be extrapolated.   The difference between the initial and the final values may then be assumed to have been introduced at that stage of the titration where the addition of a few drops of alkali caused a considerable change in the observed E.M.F.   This difference is then added to, or subtracted from, as the case may be, those readings which were taken after the marked change had taken place.   To the titration readings which have thus been adjusted, the hydrogen-ion concentration scale may be found by proportion, or by what amounts to the same thing, from the formula : Observed

E.M.F. — Initial extrapolated E.M.F. of oxygen-hydrogen cell (λ)
    = E.M.F. of corresponding N-calomel-hydrogen cell
    = $E_{cal} - E_{H_2} = 0.283 + 0.058 p$H.

For example, suppose that all that was known of the tartaric acid titration was the initial pH, 2.29, and the pH when 60 c.c. of alkali had been added, $viz.$, 11.75. The oxygen electrode compared with the normal calomel gave $+$ 0.413 and $+$ 0.073 volt respectively, and from the known pH's it is calculated that the E.M.F. of the hydrogen electrode against the normal calomel would have been $-$ 0.415 volt at the beginning and $-$ 0.961 volt at the end. Hence the extrapolated P.D. of the oxygen-hydrogen cell increased from $+$ 0.413 $-$ ($-$ 0.415) = 0.828 volt to $+$ 0.073 $-$ ($-$ 0.961) = 1.034 volt in the course of the titration, a difference of 0.206 volt. This is a considerable quantity to be divided proportionally over the whole titration as was done in the first method of calibration, and consequently produced a very unsatisfactory hydrion scale. But, as Fig. 10 shows, the greater part of this difference was introduced at the end-point. Therefore, if the difference 0.206 volt be added to each of the voltages observed after the end-point had been passed and then either a

proportional scale be affixed or calculated from $E = 0.828 + 0.283 + 0.058\, p$H, a more satisfactory calibration is obtained, save for that part of the curve corresponding to the initial alkaline solutions. The curves obtained by this procedure are given by dotted lines in Fig. 11. The tartaric acid curve is nearly coincident with the one obtained by the hydrogen electrode, and the malonic acid curve lies closer to the true curve. The oxalic curve, however, is less satisfactory.

The first method of calibration was adopted in connexion with some precipitation studies with sodium hydroxide from acid solutions of salts of either reducible metals, or which were more noble than hydrogen, and consequently made the hydrogen electrode inapplicable (Britton, *J. Chem. Soc.*, 1925, **127**, 2148). The initial pH's were calculated from the concentrations of acids in which the salts had been dissolved. Salts solutions of the metals : mercuric, cadmium, lead, silver, cupric, uranium, ferric were studied, and in all cases, the electrode furnished an excellent method of detecting when changes in pH occurred. The approximate pH scales which were assigned to the observed voltages were of reasonable accuracy, with the exception of that referring to the precipitation of silver oxide for which the extrapolated values of λ at the beginning and the end differed by 0.17 volt. The error was introduced in the E.M.F's registered during the precipitation with the consequence that the precipitation pH appeared to be about 6, instead of between pH 9 and 10.

CHAPTER VI.

METAL-METALLIC OXIDE ELECTRODES.

EFFORTS have been made recently to utilise oxidisable metals as electrodes to indicate changes in pH. Thus Baylis (*J. Ind. Eng. Chem.*, 1923, **15,** 852) tested river water, pH 6·5-8·6, with a tungsten wire electrode, using a suitably-opened 40-watt lamp as vessel and the tungsten filament as electrode, and Uhl and Kestranek (*Monatsh.*, 1923, **44,** 29) and Kolthoff and Hartong (*Rec. Trav. Chim.*, 1925, **44,** 113) have used antimony, the latter workers in presence of antimony trioxide, to follow changes in hydrogen-ion concentration during titrations. If a suitable metal could be found, such an electrode would be of considerable technical use. The behaviour of these electrodes is due to the presence or formation of insoluble hydroxides. An electrode occasionally used for the measurement of hydroxyl-ion concentration is that of mercury immersed in a solution containing a suspension of mercuric oxide. The E.M.F. of a mercury electrode in contact with a solution containing mercuric-ions is

$$E = \epsilon_{Hg} + \frac{0 \cdot 058}{2} \log [Hg^{\cdot\cdot}],$$

but in a solution in which mercuric oxide is insoluble, $[Hg^{\cdot\cdot}]$ is determined by the solubility product $S = [Hg^{\cdot\cdot}] [OH']^2$, and

therefore $\qquad [Hg^{\cdot\cdot}] = \dfrac{S}{[OH']^2} = \dfrac{S}{K_w^2} \times [H^{\cdot}]^2,$

whence $\qquad E = \epsilon_{Hg} + \dfrac{0 \cdot 058}{2} \log \dfrac{S}{K_w^2} + \dfrac{0 \cdot 058}{2} \log [H^{\cdot}]^2$

$\qquad\qquad = $ a constant $+ \ 0 \cdot 058 \log [H^{\cdot}]$ at 18° to 20° C.

$\qquad\qquad = E' - 0 \cdot 058 \ p$H.

This equation is independent of the valency of the metal, and thus it appears on theoretical grounds that a metal electrode, dipping into a solution in which some of its oxide is placed so as to saturate the solution with the hydroxide, should set up potentials depending upon the concentration of hydrogen-ions and some constant function, involving both the electromotive activity of the metal and the solubility product of its hydroxide. Its potential

should therefore alter by 58 millivolts for a change in hydrogen-ion concentration indicated by one pH unit. The above linear relationship must be regarded as the ideal case, however, for experimental complications arise due to the solubility of the oxide, its dependence upon the size of its grain, and a certain sluggishness with which it enters into equilibrium when encountering changes in hydrogen-ion concentration. These factors affect the constancy of E', but as these fluctuations are often themselves functions of the pH attained in the solution, it is possible in the case of certain metals to construct calibration curve connecting true pH values and observed potentials.

These metal-metallic oxide electrodes are, in effect, oxygen electrodes in which the precise pressure of oxygen is determined by the tendency of the oxide to dissociate into free oxygen and the metal at the particular temperature. Thus, G. N. Lewis (*J. Amer. Chem. Soc.*, 1906, **28**, 158) calculated from the observed pressures of oxygen of silver oxide at high temperatures that the pressure of oxygen which originates from silver oxide at 25° C. is equal to 5×10^{-4} atmospheres, whilst Glasstone (*J. Chem. Soc.*, 1921, **119**, 1924) found from E.M.F. measurements of a lead, lead oxide electrode, by assuming the E.M.F. of the oxygen-hydrogen cell to be 1·226 volts that the dissociation pressure of oxygen from lead monoxide was $4·2 \times 10^{-67}$ atmospheres at 25° C.

If we assume for the present that the oxygen electrode is reversible, then the difference in potential which exists between two oxygen electrodes having different oxygen pressures immersed in a solution whose oxygen-ions exert an osmotic pressure of p atmospheres could be accounted for on the grounds that the oxygen-ions at the surfaces of the two electrodes would have different electrolytic solution pressures. These solution pressures of oxygen-ions would bear a similar relationship to the pressures of the gaseous oxygen surrounding the platinum electrodes, as was the case with the hydrogen electrode as shown on page 50. Hence, the electrode reaction : $O_2 \rightleftharpoons 2O''$, could be expressed as

$$\frac{[O'']^2}{[O_2]} = \frac{[\text{electrolytic solution pressure}]^2}{[\text{gaseous pressure}]} = \frac{P^2}{\pi} = K,$$

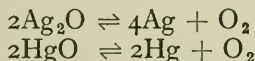and therefore the potential of a single oxygen electrode, at pressure π, would be

$$E_{O_2} = \frac{RT}{2F} \cdot \log_e \frac{P}{p} = \frac{RT}{2F} \cdot \log_e \frac{\sqrt{K \times \pi}}{p}.$$

(*N.B.*—This expression is the reciprocal of that given for the hydrogen electrode, because oxygen forms anions—see p. 11.)

If the pressure at one oxygen electrode were equal to one atmosphere, and that at the other were π atmospheres, then the E.M.F. of the cell would be

$$\begin{aligned}
\text{E.M.F.} &= \text{E}_{1\text{ atmos.}} - \text{E}_{\pi\text{ atmos.}} \\
&= \frac{\text{RT}}{2\text{F}} \log_e \frac{\sqrt{\text{K} \times 1}}{p} - \frac{\text{RT}}{2\text{F}} \log_e \frac{\sqrt{\text{K} \times \pi}}{p} \\
&= \frac{\text{RT}}{4\text{F}} \log_e \frac{1}{\pi} = \frac{0 \cdot 058}{4} \log \frac{1}{\pi} \text{ at } 18° \text{ to } 20° \text{ C.}
\end{aligned}$$

If therefore a metal-metallic oxide electrode be substituted for the oxygen electrode of pressure π such that π is the dissociation pressure of the oxide, then the electrode process could be represented, for example, as

$$2Ag_2O \rightleftharpoons 4Ag + O_2$$
$$2HgO \rightleftharpoons 2Hg + O_2$$

in the case of the Ag | Ag_2O and Hg | HgO electrodes respectively. According to G. N. Lewis's computation the dissociation pressure of silver oxide is 5×10^{-4} atmospheres at $25°$ C., and therefore the potential of a silver-silver oxide electrode in any solution will be

$$0 \cdot 0591 \log \frac{1}{5 \times 10^{-4}} = 0 \cdot 049 \text{ volt}$$

less positive than the hypothetical reversible oxygen electrode. Despite some unknown disturbing influences on the potential of the Ag | Ag_2O electrode, the author found that by using *freshly* precipitated oxide in sodium hydroxide solutions above pH $11 \cdot 4$ the potentials which were readily attained were $1 \cdot 167$ volts more positive than those of hydrogen electrode in the same solution at $20°$ C. If we add $0 \cdot 049$ volt, which is also true for $20°$ C., to $1 \cdot 167$ volt, we obtain $1 \cdot 216$ volt as that of the oxygen-hydrogen cell,—a value a few millivolts lower than the extrapolated value of Nernst and Wartenberg.

Glasstone found that the Pb | PbO electrode was at $25°$ C. $0 \cdot 247$ volt more positive than the hydrogen electrode would have been when in equilibrium with the same alkali solution, *viz.*, N-NaOH. This is equivalent to $1 \cdot 226 - 0 \cdot 247 = 0 \cdot 979$ volt below the potential of the hypothetical reversible oxygen electrode. Unfortunately this electrode is not applicable for the measurement of hydrogen-ion concentrations on account of the solubility of lead oxide in alkaline solutions.

The mercury-mercuric oxide electrode has been used for the determination of the concentration of hydrogen-ions and also for

following pH changes in alkaline solutions. According to All-
mand (*Zeitsch. Elektrochemie*, 1910, **16**, 263 ; see p. 30) it is at
18° C. always 0·925 volt more positive than the corresponding
hydrogen electrode, and thus it appears that the potential of the
mercury-mercuric oxide electrode

$$E_{Hg/HgO} = 0·925 + 0·058 \log [H^·].$$

By comparing this formula with that evaluated on page 79, we
see that the constant, 0·925, might have been calculated from

$$\epsilon_{Hg^{··}} + \frac{0·058}{2} \log \frac{S}{K_w^2},$$

to which it is equal. Of the quantities involved, ϵ, the nor-
mal potential of divalent mercury is equal to $+ 0·86$ volt,
$K_w = 10^{-14·13}$ at 18° C., and $S = [Hg^{··}][OH']^2$. The value of
the solubility product may be calculated from the potential of
the Hg | HgO electrode when immersed in solutions of known
pH from

$$E = \epsilon_{Hg^{··}} + \frac{0·058}{2} \log \frac{S}{K_w^2} + 0·058 \log [H^·].$$

If we take Donnan and Allmand's values of E in 0·1 N-NaOH,
pH $= 13·07$, $E = 0·169$ volt, and in 1·0 N-NaOH, pH $= 14·05$,
$E = 0·114$ volt, we find that $S = 1 \times 10^{-26}$ (approx.) $=$
$[Hg^{··}][OH']^2$ in each case. By knowing that the mercury-mer-
curic oxide electrode establishes a potential, 1·232—0·925=0·307
volt less than the hypothetical reversible oxygen-electrode would
have done in the same solution, Allmand calculated that the
electrode exercised an oxygen pressure of 6×10^{-22} atmosphere,
i.e., the dissociation pressure of mercuric oxide at 18° C. Hence
we conclude that this particular electrode behaves reversibly
as an oxygen electrode and may be used to calculate the pH of
alkaline solutions. Its nature imposes upon it certain limitations.
It can only be used in alkaline solutions for the oxide dissolves
in acids. Another disadvantage arises from the tendency of re-
duction of mercuric-ions to mercurous-ions at the expense of the
mercury, thus

$$Hg + Hg^{··} \rightleftharpoons 2Hg^·$$
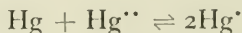
with the formation of black mercurous oxide, though this does
not occur in the more alkaline solutions as it is known that the
Donnan-Allmand standard electrodes remain of constant potential
for long periods of time. This is because the concentration of
mercurous-ions is, at such pH's, vanishingly small. Pinkhof

(*Diss.*, *Amsterdam*, 1919) has shown that chloride-ions interfere with the electrode by accelerating reduction to form calomel. If no chloride-ions be present the electrode can be used above pH 8, below which both reduction and solution occur. If the concentration of chloride-ions be 10^{-2} gram-ions per litre, then the electrode can only be used above pH 9, if $[Cl'] = 10^{-1}$, above pH 10, and if $[Cl'] = 1$ Molar, above pH 11. Pinkhof showed that electrometric titrations can be performed with the electrode, but on account of the alkaline range of utility, he found it necessary to employ fairly concentrated solutions and to titrate solutions to which excesses of alkali had been added in order to get the inflection within the range of pH. In this way he was able to estimate magnesium in the presence of calcium by titration with N-HNO_3. Phosphates, pyrophosphates, borates, and alkaloids could also be estimated.

Many other metal-metallic oxides have been investigated. From what has been written it is probable that silver-silver oxide is useless, so also is copper-cupric oxide, for as found by the author (*J. Chem. Soc.*, 1925, **127**, 2796) reduction readily takes place. Certain metals are so readily oxidisable that they become covered with an oxide film as soon as the pH of the salt solutions in which they may be immersed is increased, and then they function, often irregularly, as hydrogen electrodes. This applies to aluminium, zinc, cadmium, and antimony. Heyrovský (*J. Chem. Soc.*, 1920, **117**, 35) proved that the action taking place at the surface of an aluminium electrode was due to the formation of a skin of aluminium hydroxide, which owing to its extremely small solubility product, *viz.*, 10^{-33}, resisted to a very great extent the action of acids, so that the potential of the electrode was determined directly by the hydroxyl-ion concentration, and only by the aluminium-ion concentration inasmuch as it was permitted by the solubility product equilibrium. Uhl and Kestranek state that antimony contains sufficient oxide, but Kolthoff and Hartong prefer to place some antimony trioxide in the solution being examined. They found that at $14°$ C. the change in voltage per pH up to 5 was somewhat less than 57 millivolts, as required by the formula, but above pH 9 the variation became a little greater, but not as great as 57 millivolts. Because antimony oxide is not appreciably soluble in a decinormal solution of either hydrochloric acid or sodium hydroxide solution, the electrode has a wide range of applicability. The antimony oxide is prepared by dissolving metallic antimony in nitric acid, evaporating to dryness, and gently igniting. Kolthoff and Hartong found this electrode to give very reproducible potentials, and by interpolation on an E.M.F. — pH curve, drawn

from observations made in a series of buffer solutions, satisfactory pH values were obtained. The following data are taken from Kolthoff and Hartong's paper, which show the variation in potential of an antimony-antimony oxide electrode against the normal calomel electrode at $14°$:—

TABLE 12.

E.M.F's of Sb | Sb_2O_3 | SOLUTION | N^+-CALOMEL AT $14°$ C.

pH .	.	0·97	1·05	1·2	2·87	3·0	4·0	4·9
E.M.F. .	.	0·087	0·089	0·102	0·182	0·190	0·236	0·279

pH .	.	5·0	5·7	6·0	7·0	8·24	9·0
E.M.F. .	.	0·282	0·330	0·327	0·374	0·457	0·493

pH .	.	9·36	10·14	11·3	12·25	13·2
E.M.F. .	.	0·512	0·557	0·616	0·660	0·741

From the calibration curve plotted from these data Kolthoff and Hartong found that the difference in potential between the antimony electrode and the normal calomel for solutions up to pH 5, could be expressed as

$$E_{cal} = 0·0415 + 0·0485 \, p\mathrm{H},$$

and when immersed in solutions of pH 9 and above,

$$E_{cal} = 0·009 + 0·0536 \, p\mathrm{H}.$$

Compared with the Arbitrary Zero, $viz.$, the Normal Hydrogen Electrode, these expressions become

$$E_h = 0·2415 + 0·0485 \log [\mathrm{H}^{\cdot}]$$

and

$$E_h = 0·274 + 0·0536 \log [\mathrm{H}^{\cdot}]$$

In the region of pH 5 — 7 variable results were obtained. The following data give some idea of the accuracy obtainable by this method : using the hydrogen electrode the pH of beer was 4·30, whereas by the antimony electrode it was 4·32 ; by the former method a sample of milk had a pH of 6·90 whilst the antimony electrode gave 6·84.

This electrode is particularly serviceable for titration work, $e.g.$, solutions of acids such as hydrochloric, sulphuric, nitric, perchloric, acetic, oxalic, and tartaric, and also alkaline solutions containing oxidising agents, $e.g.$, permanganate and chromates. Stirring is necessary either by means of a motor or some indifferent gas, $e.g.$, nitrogen. If E.M.F's are desired from which accurate pH values can be found, antimony oxide should be present in the

solution, though this is unnecessary for titrimetric estimations. It should be stated that tartaric acid, though it may be titrated with this electrode as indicator, has a pronounced solvent action on the oxide through the formation of a soluble complex tartrate solution, and thereby lessens the inflection and voltages, so that pH values cannot be found. Similar disturbing influences on potentials are produced by those strong oxidising agents, *e.g.*, permanganate, which bring about the oxidation of the oxide to antimonic oxide. Further investigation by Roberts and Fenwick (*J. Amer. Chem. Soc.*, 1928, **50**, 2125) has shown that the satisfactory functioning of the antimony-antimony oxide electrode occurs when the oxide present is in the stable form, *viz.*, cubic, and not in the unstable orthorhombic modification, usually obtained by the hydrolysis of the trichloride, and when dissolved oxygen has been excluded.

Tungsten–Manganic Oxide Electrode.

As previously stated Baylis showed that tungsten wire behaved as a metal-metallic oxide electrode so that it could be used for investigating changes in hydrogen-ion concentration of river water. This work has been followed up by Parker (*J. Ind. Eng. Chem.*, 1925, **17**, 737), who also took advantage of the observation of Thompson and Crocker (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 167) that manganese dioxide will act as an oxygen electrode. Working with different metals and oxides not in immediate

### TABLE 13.

E.M.F's of Metal | Oxide. Buffer Solution | H_2
(Parker).

Electrode.	Buffer Solution.			
	Phthalate pH = 3·92.	Phosphate pH = 6·35.	Borate, NaCl pH = 8·25.	Borate pH = 9·07.
W—Co_2O_3 . . .	0·387	0·480	0·501	0·508
W—MnO_2 . . .	0·448	0·448	0·512	0·516
W—Mn_2O_3 . . .	0·402	0·486	0·501	0·502
W—Mn_2O_3, treated .	0·450	0·462	0·466	0·464
W, bare . . .	0·371	0·410	0·457	0·453
W, treated . . .	0·355	0·410	0·435	0·433
Pt—Mn_2O_3 . . .	0·981	1·016	1·015	1·016
Pt, platinised . .	0·928	0·940	0·945	0·940
Pt, platinised—Co_2O_3 .	0·918	0·952	0·952	0·954
Au, platinised—Mn_2O_3 .	0·965	0·976	0·971	0·967
Pt, platinised—Mn_2O_3 .	0·968	0·974	0·970	0·969

contact, it was found that very often the electrode ceased to func-
tion, but when the oxide was brought into intimate contact with
the electrode metal this difficulty was overcome. Table 13 gives
the results obtained when such electrodes were placed in buffer
solutions of different pH values. The E.M.F's are referred to the
potentials of the hydrogen electrode when in equilibrium with the
various solutions.

The table shows that the only two electrodes to give a really
satisfactory relationship to the hydrogen electrode potentials
throughout the pH range from 4 to 9 were platinised gold and plat-
inum electrodes in contact with manganese sesquioxide. Many
of the different electrodes gave constant values in alkaline solutions
and could therefore be used in solutions greater than 8. Though
tungsten cannot be regarded as an unattackable metal and therefore
to behave as does platinised platinum or gold, Parker found that
when tungsten electrodes were placed in a strongly alkaline buffer
solution their potentials drifted for several days but ultimately
approached a definite value. Electrodes treated in this way may,
as shown in Table 13, be used in solutions down to pH 4. The
effect of this alkali treatment lasts for two or more weeks during
which time Parker states, the electrodes can be used in flowing
solutions in conjunction with a self-recording potentiometer. One
advantage of the tungsten-manganic oxide electrode appears to
rest in its resistance to " poisoning." As may be expected from
Table 13, the E.M.F's of these electrodes is not a linear function
of pH, and in order to ascertain pH values it is necessary to cali-
brate the potentials of the electrode in solutions of known pH
values. These electrodes do not function in acid solutions below
pH 4. They have been patented by the Leeds and Northrup Co.
(Parker and Dannerth, *J. Ind. Eng. Chem.*, 1925, **17**, 637 ;
U.S.P. 1,513,558/1924), and have been used in the sugar and
other industries (see Chapter XXIV). As the electrodes require
20-30 minutes in which to attain equilibrium, they are placed in
position sometime before being incorporated in the potentiometer
circuit.

It appears that manganic oxide in contact with a platinised
electrode tends to supply it with oxygen, thus

$$4Mn(OH)_3 \rightleftharpoons 4Mn(OH)_2 + O_2 + 2H_2O,$$
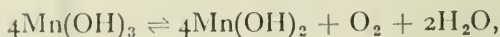
so that the pressure of oxygen,

$$[O_2] = \frac{K[Mn(OH)_3]^4}{[Mn(OH)_2]^4},$$

and therefore if the ratio of the concentrations of the two dissolved hydroxides remained constant, then we see that the electrode would function as an oxygen electrode under a constant pressure of oxygen gas.   The concentration of manganous hydroxide will be kept extremely small on account of the ease with which it becomes oxidised to the hydroxide of higher valency, but as this oxidation process is a question of the prevailing pH and also as the higher oxide becomes soluble at a pH value below 4, it is seen that the electrode is useless in the more acid solutions.   It is therefore in neutral and alkaline solutions where the electrode may be expected to function best.   Taking the tungsten-manganese oxide electrode as 0·46 volt more positive than the corresponding hydrogen electrode, we see that it will be 0·77 volt less than that of the hypothetical oxygen electrode in equilibrium with the same solution, whence it follows that the effective oxygen pressure in the electrode is 10^{-53} atmospheres.   This explanation is comparable with that applied to the quinhydrone electrode.   The disregard of the fact that the tungsten electrode is attackable is not justifiable, especially as gold and platinum manganic oxide electrodes are each about 0·5 volt more positive.   There must be therefore a more involved series of equilibria established between any oxides of tungsten, formed at the electrode surface, and those of manganese.   This type of electrode, in spite of being in its preliminary stages of development, has already been found of service in water purification, treatment of boiler feed-water, sugar refining, and sewage disposal.

CHAPTER VII.

THE GLASS ELECTRODE.

Haber's Glass Electrode.

On account of the difficulties encountered in the measurement of the concentrations of hydrogen-ions of solution, and particularly those of coloured biological fluids for which colorimetric methods are inapplicable, continued efforts are being made to develop new electrometric methods. Since Haber and Klemensiewicz (*Z. physikal. Chem.*, 1909, **47**, 385) in 1909 first showed that the change in potential between a glass interface and a solution could be utilised as a means of following the variation in pH in acid-alkali titrations, several valuable researches have been carried out, and thanks to the efforts of Mrs. Kerridge and W. S. Hughes the glass electrode now provides a valuable method for the accurate determination of hydrogen-ions.

It might be of interest to trace briefly the history of the glass electrode. As the result of an idea thrown out by Nernst (*Z. physikal. Chem.*, 1892, **9**, 137) regarding the potential difference which should exist at the boundary between a mixed crystal and its saturated solution, Haber conceived the idea that potentials should exist at glass-aqueous solution interfaces. Freundlich and Rona (*Berlin Akad. Ber.*, 1920, 397) confirmed Haber and Klemensiewicz's observations, whilst both Hughes (*J. Amer. Chem. Soc.*, 1922, **44**, 2860 ; *J. Chem. Soc.*, 1928, 491) and von Steiger (*Z. Elektrochemie*, 1924, **30**, 259) amplified the manipulative details and compared glass electrode potential data with those given by the hydrogen electrode in the same solutions. The problem of obtaining suitable glass, as regards the functioning of the electrode as if it were made of hydrogen and also its electrical resistance, has been investigated by Horowitz (*Z. Physik*, 1923, **15**, 369), Schiller (*Ann. Physik*, 1924, **74**, 105), and recently by Hughes (*loc. cit.*). The glass electrode now finds a place in the Biochemical and Physiological Laboratories of University College, London, in connexion with pH measurements of such substances as blood and minced muscles, and many valuable papers have originated therefrom dealing with

its manipulation and use (Brown, *J. Sci. Instr.*, 1924, **2**, 12 ; Kerridge, *Biochem. J.*, 1925, **19**, 611 ; *J. Sci. Instr.*, 1926, **3**, 404 ; Baylis, Kerridge and Verney, *J. Physiol.*, 1926, **61**, 448). In the following discussion two forms of glass electrode will be described, one designed by Kerridge, and now, together with the necessary accessories, placed on the market by the Cambridge Instrument Co., London, and a more simple form introduced by Hughes.

Theory of Glass Electrode.

Much of the theory underlying the potential of a glass electrode is somewhat a matter of conjecture, for the potential depends upon the composition and nature of the glass inasmuch as these factors seem to determine with which type of ion in a solution it will enter into a state of equilibrium. Table 14 gives the analyses of various glasses studied by Hughes :—

TABLE 14.

COMPOSITIONS OF GLASSES SUITABLE AND UNSUITABLE FOR GLASS ELECTRODES.

Constituent.	Suitable.		Unsuitable.			
SiO_2	71·83	69·75	70·62	67·56	66 88	72·19
Al_2O_3	0·44	1·04	3·23	6·53	4·60	8·96
TiO_2	—	—	Trace	Trace	Trace	—
Fe_2O_3	0·04	0·05	0·11	0·13	0·08	—
MnO	—	0·21	Trace	0·17	Trace	—
CaO	8·36	11·26	7·58	6·54	6·76	0·08
MgO	Trace	Trace	0·25	—	0·81	—
Na_2O	18·83	16·54	15·48	15·82	15·48	18·79
K_2O	—	0·66	2·62	3·34	5·56	—
SO_3	0·22	0·34	—	—	—	—
Sb_2O_3	—	0·22	—	—	—	—
Conductivity	Excellent	Very good	Good	Poor	Very poor	Good
Change in voltage per 1 *p*H, compared with hydrogen electrode E.M.F. (*p*H 0-10)	95-98%	95 (?) %	92%	88%	—	24-27%

It will be observed that the glasses which conducted electricity well had both high sodium oxide and calcium oxide contents, but that in the two glasses from which satisfactory electrodes could be made there was comparatively a small percentage of alumina, much ·

less than 2 per cent. It appears therefore that the less alumina a glass contains the better it will be for glass electrode work ; also that a high soda content enhances the conductivity, whereas potash seems to decrease it. Hughes states that the glass represented by the first set of analyses had such a high conductivity that electrostatic shielding of the cell was unnecessary, and in addition, the electrode potential was scarcely influenced by large variations in sodium-ion concentration, provided that the pH was less than 9. If boric oxide be present in a glass, then it may function as was found by Horowitz and Schiller (*loc. cit.*) as both a sodium and hydrogen electrode. Hence in borosilicate glasses the sodium content partly determines the potential of the resulting glass electrodes, whereas soda-lime glasses containing no boric oxide and relatively small quantities, less than 2 per cent., assume potentials which over the range pH 0 to pH 10 are almost a linear function of the pH of the solutions in which the electrodes are immersed. This will be evident from the last line in Table 14.

In developing a tentative explanation of those glass electrodes which respond to changes in hydrogen-ion concentration in a manner analogous to that of the hydrogen electrode, we shall regard the soft soda glass as being a solid solution of soda and silica more or less in the state of chemical combination and an excess of silica, such that when a thin bulb of glass is immersed in an aqueous solution a certain amount of water will be attracted into the glass phase, through adsorptive processes, and tend to combine with the free silica, thereby imparting to it acidic properties. Such a cause may be attributed to the fact that a considerable amount of water is adsorbed by glass in contact with acids, recently observed by Frazer, Patrick and Smith (*J. Physical Chem.*, 1927, **31**, 897). Hughes considers that his " results are best explained on the view that the hydrogen-ion concentration in the glass phase is held relatively constant by the buffer action of the glass," which " action *prevents* ionic exchange between the glass phase and the solution from altering the hydrogen-ion concentration in the glass, which is thus maintained relatively constant in spite of the exchange of ions with the solution." The author's hydrogen electrode titration curves of silicic acid (pp. 414 and 312, *J. Chem. Soc.*, 1927, 425) show that alkalis, *e.g.*, NaOH and the hydroxides of the alkaline earths, enter into perceptible combination with silicic acid over the extensive pH range above pH 6. Whilst the curve corresponding to the action of sodium hydroxide upon silicic acid does not permit of the calculation of satisfactory dissociation constants, K_1 and K_2, of the hypothetical metasilicic acid, the curve resolves itself into two sections in which pronounced

buffer actions on the hydrogen-ion concentration are produced. The first stage refers to the neutralisation reaction :

$$H_2SiO_3 + NaOH \rightarrow NaHSiO_3,$$

during which the hydrogen-ion concentration is confined mainly within the range pH 9–10·4, thereafter further addition of alkali produces a fairly rapid diminution in hydrogen-ion concentration. It will be remembered that solid sodium silicates only become readily soluble in water when their soda contents have become sufficiently great, so much so that glasses containing a great excess of silica possess no solubility in water, except when the water has been rendered strongly alkaline. Through the action of the soda on the silica in the surface layers, silicates with higher sodium contents become formed and solution thereupon results. Hence it may be assumed that except in alkaline solutions, say above pH 10, the glass electrode will have maintained at its surface, through the absorbed water which tends to dissolve in the glass, a constant concentration of hydrogen-ions of about pH 9. This low, but definite concentration of hydrogen-ions will produce a pressure at the glass surface, comparable with the electrolytic solution pressure in the case of ordinary reversible electrodes, which in tending to oppose the osmotic pressure of hydrogen-ions already in the solution, will establish a difference in potential between it and the solution. As glass might be considered as a solution of extremely high viscosity, ions will only be able to travel across it with great difficulty, especially as the resistance of the thinnest glass membrane is of the order of 50 megohms. The diffusion of water molecules into the membrane will facilitate the motion of ions through the glass film, and as hydrogen-ions and hydroxyl-ions are the fastest in aqueous solutions it is probable that they will also be the fastest through the glass-water solution, and consequently it follows that these ions alone will carry the current across the diaphragm. If two solutions having different concentrations of hydrogen-ions are separated by such a wall, then there should exist a difference in potential between them urging the movement of hydrogen-ions through the glass in one particular direction.

We shall now consider this potential difference. Suppose we have the system :—

	Solution I	Glass	Solution II
Concentration :	$[H^{\cdot}]_I$	$[H^{\cdot}]_G$	$[H^{\cdot}]_{II}$
		A B	
	pH_I		pH_{II}
Osmotic pressure :	p_I	P	p_{II}
		E_I E_{II}	

The nature of the components of the glass, through their buffer action, tend to maintain a constant pressure, P, of hydrogen-ions in the glass. We have, therefore, in effect two solutions in equilibrium with the same hydrogen electrode. Its potential, E_I, with respect to Solution I will be equal to

$$E_I = \frac{RT}{F} \log_e \frac{p_I}{P} = \frac{RT}{F} \log_e \frac{[H^\cdot]_I}{[H^\cdot]_G}$$

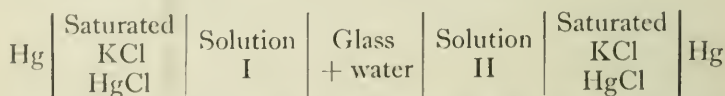whereas its potential, E_{II}, with regard to Solution II, will be

$$E_{II} = \frac{RT}{F} \log_e \frac{p_{II}}{P} = \frac{RT}{F} \log_e \frac{[H^\cdot]_{II}}{[H^\cdot]_G}.$$

Hence $E_I - E_{II}$ is the difference in potential between Solution I and Solution II, and therefore the E.M.F. tending to force hydrogen-ions across the glass barrier,

$$\begin{aligned}
\text{E.M.F.} &= \frac{RT}{F} \log_e \frac{[H^\cdot]_I}{[H^\cdot]_G} - \frac{RT}{F} \log_e \frac{[H^\cdot]_{II}}{[H^\cdot]_G} \\
&= \frac{RT}{F} \log_e \frac{[H^\cdot]_I}{[H^\cdot]_{II}} \\
&= 0 \cdot 0001984T \log \frac{[H^\cdot]_I}{[H^\cdot]_{II}} \\
&= 0 \cdot 0001984T \, (pH_{II} - pH_I) \\
&= 0 \cdot 058(pH_{II} - pH_I) \text{ at } 18° \text{ to } 20° \text{ C.}
\end{aligned}$$

It will be observed that this potential difference does not involve the postulated concentration of hydrogen-ions in the glass. Moreover, the change in the potential difference between two solutions having different hydrogen-ion concentrations should be 58 millivolts for each pH unit difference. Table 14 shows that these variations in E.M.F. are approximately true of the satisfactory glass electrodes—over the pH range 0-10. Above pH 10 the solvent action of the alkali upon the glass becomes apparent in that it disturbs the buffer action within the glass and so alters its hydrogen-ion " osmotic " pressure.

In order to measure the potential difference between the two solutions, Mrs. Kerridge employs two saturated calomel electrodes with the tip of one dipping into one solution and that of the other in the second solution. The cell thus made is

$$\text{Hg} \left| \begin{array}{c} \text{Saturated} \\ \text{KCl} \\ \text{HgCl} \end{array} \right| \begin{array}{c} \text{Solution} \\ \text{I} \end{array} \left| \begin{array}{c} \text{Glass} \\ + \text{ water} \end{array} \right| \begin{array}{c} \text{Solution} \\ \text{II} \end{array} \left| \begin{array}{c} \text{Saturated} \\ \text{KCl} \\ \text{HgCl} \end{array} \right| \text{Hg}$$

and as the contact potentials introduced where the saturated calomel electrodes are connected with the solutions are very small

and act in opposition to one another, it follows that the observed
E.M.F. of the cell will be produced by the fall in potential between
Solution I and Solution II.   In the Hughes' type of glass electrode
the cell is set up in the following way :—

$$\text{Hg} \left| \begin{array}{c} \text{Saturated} \\ \text{KCl} \\ \text{HgCl} \end{array} \right| \begin{array}{c} \text{Solution} \\ \text{I} \end{array} \left| \begin{array}{c} \text{Glass} \\ \text{+ water} \end{array} \right| \begin{array}{c} \text{Solution II} \\ \text{(N-HCl)} \\ \text{. HgCl} \end{array} \left| \text{Hg} \right.$$
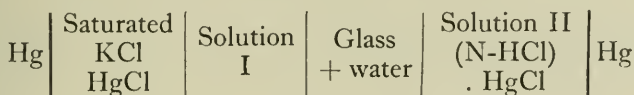
there being no attempt made to eliminate extraneous potentials, but
the potentials introduced are of constant value, namely, that of the
saturated calomel electrode and that established between mercury
and a N-HCl solution saturated with calomel.   The contact
potential between the saturated calomel electrode and the solution
will be negligibly small.   In the Kerridge cell, therefore, the
E.M.F. $= 0 \cdot 0001984 \text{T} \log \dfrac{[\text{H}^{\bullet}]_{\text{I}}}{[\text{H}^{\bullet}]_{\text{II}}}$ but in the Hughes' cell, the
E.M.F. observed is the direct outcome of the potential difference
between the saturated KCl and N-HCl calomel electrodes together
with the E.M.F. given by the Kerridge cell.   Let the constant
difference in potential between the two different calomel half-
elements used in the Hughes' arrangement be a volt, then the
observed E.M.F. of the cell will be given by

$$\text{E.M.F.} = a + 0 \cdot 0001984 \text{T} \log \frac{[\text{H}^{\bullet}]_{\text{I}}}{[\text{H}^{\bullet}]_{\text{II}}},$$

but as $[\text{H}^{\bullet}]_{\text{II}}$ refers to the hydrion concentration of N-HCl solution
saturated with calomel, *i.e.*, solution II, we see that this will be
constant in value, and

$$\therefore \text{E.M.F.} = b + 0 \cdot 0001984 \text{T} \log [\text{H}^{\bullet}]_{\text{I}}$$

where b is a constant involving a and the $[\text{H}^{\bullet}]_{\text{II}}$ term.   Hence
on theoretical grounds, whereas it is only necessary to know the
pH of one of the solutions present in the Kerridge cell in order
to calculate the pH of the other solution, with the Hughes'
arrangement the constant b must first be evaluated.   This can
be done by placing in the cell a solution of known pH and observing
the E.M.F. established.   Actually, on account of the possibility
of the erratic behaviour of the glass electrode, *e.g.*, through slug-
gishness in the attainment of equilibrium with the solution under
test, the observed E.M.F's may not always be represented by the
foregoing expressions.   Moreover, there is always a so-called
asymmetry E.M.F. between the two sides of the glass membrane
itself irrespective of the solutions in contact with them.   In our

considerations we have assumed that the " osmotic " pressure of the hydrogen-ions was the same on both sides. In good glass electrodes this asymmetry E.M.F. is fairly low and assumes a steady value within a few hours of being placed in contact with solutions. Though the quality of the glass is of some importance in this connexion, much depends upon the blowing and thickness of the glass membrane, for different glass electrodes can be prepared from the same glass which give quite different E.M.F's. This asymmetry E.M.F., through its failure to acquire an absolutely constant value, probably explains why the E.M.F. of a glass cell corresponding to a given change in pH of the solution in contact with a glass diaphragm varies from cell to cell, and from day to day in the same cell. Hence, it is necessary to standardise the glass cell at least once each day. In the Kerridge form this is done by inserting a buffer solution of known pH in the vessel in which the solution of unknown pH is ordinarily placed. Hence by knowing the pH values of Solution I and Solution II, and the E.M.F. of the cell, the extent by which the formula given above may be expected to be in error for any particular day may be calculated ; suppose it to be equal to E_a, then

$$E_a = \text{E.M.F.}_{\text{(observed)}} - \text{E.M.F.}_{\text{(calculated)}}$$

and therefore

$$\text{E.M.F.}_{\text{(observed)}} = 0 \cdot 0001984 T \log \frac{[\text{H}^{\cdot}]_I}{[\text{H}^{\cdot}]_{II}} + E_a$$
$$= E_a + 0 \cdot 058 \, (p\text{H}_{II} - p\text{H}_I) \text{ at } 18° \text{ to } 20° \text{ C.}$$

For this purpose Mrs. Kerridge recommends a M./20-solution of potassium hydrogen phthalate, which has a pH of $3 \cdot 97$ at $18°$ C., and the change in pH with temperature is very small. Such a solution will remain at pH $3 \cdot 97$ for at least a fortnight if kept in a waxed bottle.

Hughes, on the other hand, considers it better to check the measurement of the pH of the solution under examination by measuring the E.M.F's produced by two standard buffer solutions, one of slightly lower pH and the other of slightly higher pH than the solution, when replacing the unknown solution— and then to interpolate the required pH from the latter voltages. In this way, errors due both to the fact that the glass cell does not readily give reproducible results and to the asymmetry E.M.F. will probably be eliminated entirely.

Attention has already been directed to the glass most suitable for electrode purposes. Soft soda lime glass such as that ordinarily

found in soft glass tubing will often be found quite satisfactory. Thus Mrs. Kerridge (*J. Sci. Inst.*, 1926, **3**, 404) used most frequently a cheap German soft soda glass which was considered inferior from the glass-blower's point of view. The glass membrane should be as thin as possible, preferably between 0·025 and 0·030 mm. in its thinnest part and should never exceed 0·1 mm. The thinner the membrane the more likely is the electrode to function as a hydrogen electrode, and the more easily will the E.M.F's of the cell be measured, through the smaller resistance of the glass wall. Needless to mention the electrode must be as thin as is consistent with mechanical strength. The bulb must be as free from strain as possible and in order to minimise asymmetry E.M.F's caused by strain the glass membrane must be blown as rapidly as possible and no attempt made to work the glass. Devitrification of the membrane renders it useless as the glass then, in beginning to become crystalline, loses the electrode function which seems to be inherent in it being a supercooled liquid. The E.M.F. of the glass electrode depends upon its previous treatment. Thus if it has been cleaned by immersion in chromic acid, it will often be found necessary to place the electrode in water for a period of about two days before it can be used, as a potential will have been produced at the glass surface which, however, rapidly disappears on treatment with water. This is generally true of electrodes which are being used in either strongly acid or alkaline solutions, but in the case of the latter solutions the electrode potentials may never again become Normal. This is in accord with the fact that the glass electrode behaves abnormally in alkaline solutions through possible attack. It is advisable, therefore, not to resort to strong acids or alkalis for cleaning, but to employ gently running water. Between use, the electrode should be kept in a buffer whose pH lies in the region in which the electrode is subsequently to be used, otherwise in distilled water.

Fig. 12 is a diagram of the Kerridge type of electrode, a form which is the more convenient for general work especially as the amounts of solution required for investigation need not be more than 0·5 c.c. Because of the extremely high resistance of the glass cell, only extremely small currents can be produced and therefore every care must be taken to mount the cell on insulating material such as glass (H, Fig. 12) paraffin or orca. This type of electrode may now be obtained commercially, and Fig. 16 gives a picture of a complete outfit, including a zinc-lined box, which effectively shields the glass cell from external electrostatic fields, a suitable potentiometer and a Lindemann electrometer, required for the measurement of pH, as manufactured by the Cambridge

Instrument Co., Ltd., London. In the Kerridge cell the glass membrane is in the form of a small bulb which has been sucked back into a larger and thicker bulb, G, from the side of which two tubes project, enabling it to be readily cleaned and filled with a buffer solution, B, whose pH is accurately known. This arrangement of the glass membrane has the dual advantage that it affords protection of the exceedingly thin membrane, and that its formation by suction seems to leave less strain in the glass. The buffer solution advocated by Mrs. Kerridge comprises a solution of potassium phosphates of about pH 7. It seems preferable to use N-HCl solution, which being always of pH lower than that of the
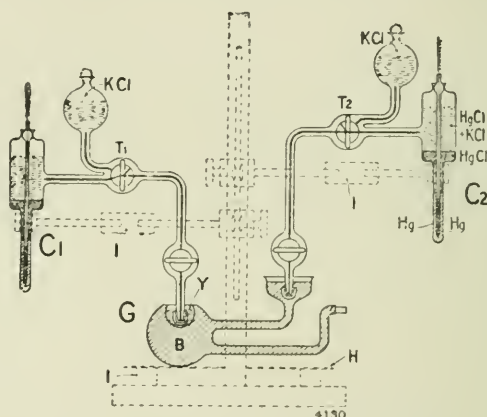
FIG. 12.—Glass Cell (Kerridge Type).
T_1, T_2 = Two-way Taps.
I = Insulators.
B = Buffer solution of known pH.
G = Glass vessel containing membrane.
Y = Solution of unknown pH.
C_1 and C_2 = Saturated Calomel Electrodes.

solutions usually tested avoids the reversal of the polarity of the electrodes of the glass cell when passing the pH of the buffer solution. This particularly applies when the electrode is used for titration work. Though the form illustrated is not suitable for this kind of test, Mrs. Kerridge has described a modified form which is suitable (*loc. cit.*). Moreover, the glass electrode functions more satisfactorily when there exists an appreciable difference in hydrogen-ion concentration on the two sides of the glass diaphragm. If the solution is likely to be oxidised by exposure to the air, or if it may suffer loss of carbon dioxide, it may be covered with a thin layer of liquid paraffin. In any case the paraffin will

serve to lessen electrical leakage across the external surface of the
electrode. The two saturated calomel electrodes, mounted on
earthed metal stands provided with adjustments for altering the
levels of the electrodes, are connected with the solutions in the
glass electrode, but in order to prevent diffusion of the potassium
chloride solution small ground caps are loosely fitted over the ends
of the connecting arms, and the two taps, which are ungreased in
the middle race, are turned off while the E.M.F. of the cell is being
measured. The added resistance introduced by these precautions
is negligible compared with that of the glass electrode.

The Hughes' form is shown in Fig. 13. This type is con-
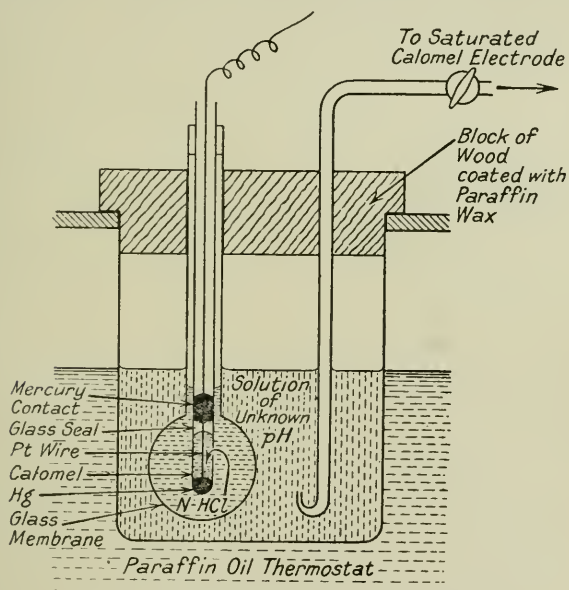
FIG. 13.—Hughes' Type of Glass Electrode.

venient for titration purposes, and, moreover, has one advantage
over the previously described pattern, in that less violent stirring
is required than is the case when a solution has to attain equilibrium
with a membrane in a cavity. It is a modification of the original
Haber electrode (*loc. cit.*, see also Horowitz, *loc. cit.*, and Hughes,
J. Amer. Chem. Soc., 1922, **44,** 2860), in which a glass bulb, with
walls 0·06 mm. thick, containing potassium chloride solution into
which dipped a platinum wire to serve as one electrode, was im-
mersed in the solution under test and this was connected to a
calomel electrode. In the Hughes' improved form the platinum

wire contact is substituted for a perforated glass tube, shown in
the diagram, at the rounded bottom of which is placed a little
mercury covered with calomel, and which thereby maintains the
N-hydrochloric acid solution, instead of KCl, contained in the
bulb in a saturated state. Contact is made with the mercury by
means of a platinum wire fused into a glass seal, connecting it
with a little mercury in the upper part of the tube, into which an
amalgamated copper wire dips. In order to avoid electrical leakage
the cell is placed in a paraffin-oil thermostat, the neck of the bulb
is held in a block of wood, coated with paraffin wax, cut to fit the
beaker as a cover, and the rim of the beaker is supported by the
paraffin-wax-coated wooden thermostat cover.

The measurement of the E.M.F. of glass cells presents a certain
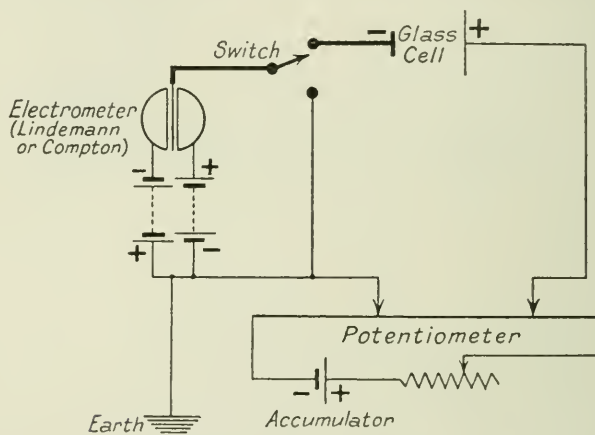
FIG. 14.—Simple Circuit for the Measurement of the E.M.F. of Glass Cell.

amount of difficulty on account of the very high resistance of
the glass membrane. Hence, the current produced will be too
small to permit the use of a capillary electrometer or a sensitive
galvanometer in connexion with the potentiometric method of
measuring potential differences described in Chapter VIII. In-
stead, resort must be made to the quadrant electrometer as a null-
point instrument. Compton, Dolazalek and Lindemann electro-
meters have been used by various workers, but without doubt the
Lindemann (*Phil. Mag.*, 1924, **67,** 578) is the more convenient
and easy to manipulate ; it possesses sufficient sensitivity for this
work, and is compact and portable. It is contained in the box
placed under the microscope in Fig. 16.

Besides being compact and robust, the Lindemann electro-

meter, as supplied by the Cambridge Instrument Co., has a stable zero and does not require levelling. It consists of a needle supported centrally at the mid-point of a quartz fibre, so that it can rotate between four cross-connected plates. The quartz fibre is fixed at both ends under tension so that the centre of rotation of the needle is fixed, and the movement of the needle is controlled by the torsion of the fibre ; the rotation can therefore be determined by observing the movement of one end of the needle through a microscope. A total magnification of 250 diameters, obtained, say, by using a microscope with 160 mm. tube length, 16 mm. objective, and 10 mm. eyepiece, enables deflections, corresponding to less than one millivolt to be observed. An objective of smaller focus than 16 mm. should not be used, as the needle could not then be sharply focussed.
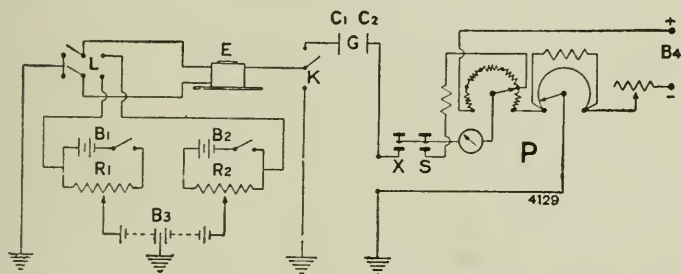
Fig. 15.—Arrangement of Wiring of Potentiometer System using Lindemann Electrometer.

E = Lindemann Electrometer.   P = Potentiometer.
B_1, B_2 = 4-volt Batteries. R_1 and R_2 = 300-ohm Potentiometers.
B_3 = 66-volt Dry Battery. B_4 = Accumulator.

The simple potentiometric system using a quadrant electrometer as the null-point indicator is given in Fig. 14. No electrical leakage must be allowed to occur between the glass cell and the electrometer, *i.e.*, along the wires indicated by heavy lines. These wires should be as short as possible and thoroughly insulated. The switch should be constructed with orca or ebonite insulation and placed on a block of clean paraffin wax. Fig. 15 shows the wiring of the potentiometer circuit using the Lindemann electrometer, employed in the Cambridge Glass Electrode Outfit (Fig. 16). It differs but slightly from that described by Mrs. Kerridge. In the Cambridge apparatus the glass cell is enclosed in a light metal box having apertures in the top and bottom, closed with microscope cover slides. The leads from the two sets of plates pass through quartz tubes to terminals at one end, while the lead from the needle is similarly carried to a terminal at the

other end. An earthing terminal enables the effect of stray electrostatic fields to be eliminated. A moisture absorption chamber, containing phosphorus pentoxide, prevents humid conditions from affecting the silica insulation. The electrometer plates are charged by means of a high-tension battery, the needle being connected in the electrode circuit. The charge required is about $+ 30$ and -30 volts on the two pairs of plates respectively. In order to ensure that the electrical and mechanical zeros of the electrometer coincide, it is necessary to adjust, to within 0·5 volt, the charges on each pair of plates for the particular instrument in use. For this purpose, a potentiometric system is put in series with the high-tension battery. The arrangement of the wiring is shown in Fig. 15. The mid-point of a 66-volt dry battery B_3 is earthed and the positive and negative terminals are connected to the movable contacts of two small 300-ohm potentiometers, R_1, R_2, across each of which is a potential difference of 4 volts. A two-way double-pole switch L enables the electrometer plates to be earthed or charged, and a two-way single-pole switch K is provided for earthing or charging the needle. The two small potentiometers and the switches are mounted together in a separate box, to the front of which the electrometer can be directly attached, terminals being fitted on the box for connecting up the high-tension battery, electrometer and electrodes. The potential difference between the two poles of the glass cell are measured by means of a potentiometer (P, Fig. 15) ; that shown at the right of the picture, Fig. 16, is the Cambridge portable potentiometer (see p. 108).

For details regarding the use of the Dolazalek and Compton electrometers reference must be made to Mrs. Kerridge's paper.

It should be stated that though the glass electrode functions best over the pH range 0 — 9, it may be employed by using two suitable buffer solutions of known pH for the determination of higher pH values quite satisfactorily by interpolating from data given by the buffer solutions. Once the fundamental needs of adjustment, insulation, shielding and standardisation have been recognised, it is only a matter of a few minutes which are required for making a determination. The electrode has already been applied successfully to biological problems, and there is every reason to believe that it will receive more general recognition especially in regard to its use in those solutions which cannot be studied by either the hydrogen or quinhydrone electrodes and which are too coloured to be dealt with colorimetrically.
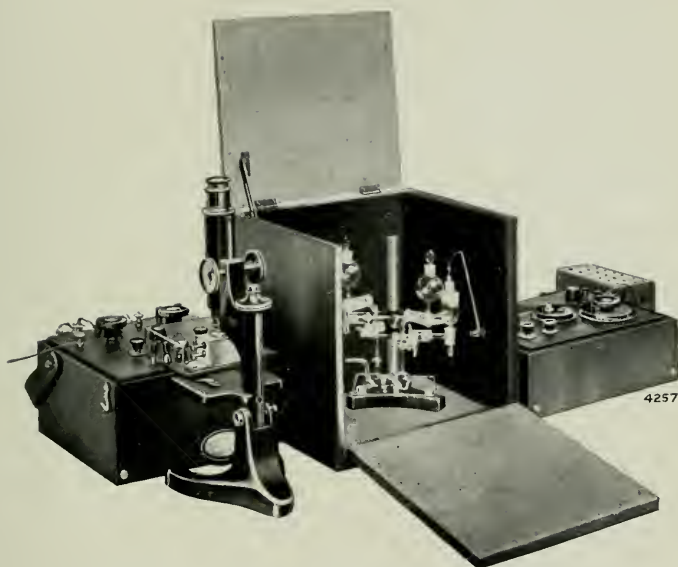
Fig. 16.—Cambridge Glass Electrode Apparatus, showing Lindemann Electrometer, Glass Electrode (Kerridge Type), and Potentiometer.
(*Block lent by* Cambridge Instrument Co., Ltd.).

CHAPTER VIII.

THE MEASUREMENT OF ELECTROMOTIVE FORCE.

HITHERTO we have considered the seats of potential difference in a cell, and have, moreover, seen that it is not possible to measure directly the potential of an electrode with respect to the solution in which it may be immersed. If we assume that the difference of potential, which originates from the contact of the two electrode solutions through the migration of ions across the boundary, can be nullified by interposing a saturated solution of potassium chloride between the two solutions, then the E.M.F. of a cell will be the result of the difference of the two electrode potentials, and if one electrode is of a constant and known value the potential of the other electrode can readily be obtained, once the E.M.F. of the cell has been ascertained. We shall now direct our attention to the methods for the determination of potential differences, but shall, in the first place, deal with the fundamental principles on which these methods are based.

Suppose we have a circuit which includes a cell, whose internal resistance is r ohms, and a voltmeter whose resistance is R ohms. The voltmeter registers a potential difference of E_v volts, which simply corresponds to the fall in potential across the terminals of the voltmeter. But Ohm's law states that the fall in potential, if measured in volts, produced when a current, measured in ampères, flows through a conductor, whose resistance is measured in ohms, is equal to the product of the current and the resistance, in other words,

$$\text{current (ampères)} = \frac{\text{potential difference (volts)}}{\text{resistance (ohms)}},$$

and therefore, the E.M.F. shown by the voltmeter, E_v, $= C \times R$, C being the current sent out by the cell. If, however, the E.M.F. of the whole circuit, E, be considered, when sufficient time has been allowed for the current in any part of the system to become constant, $i.e.$, through the external circuit and through the cell itself, we find that

$$C = \frac{E}{R + r},$$
$$E = CR + Cr.$$

Now this value, E, is derived from the chemical processes involved in the cell, and it is the quantity which it is desired to measure. Hence, as C is the uniform current circulating throughout the closed system, we see that

$$E = E_v + Cr$$

and consequently the voltmeter reading is too low by the amount Cr. Unless these quantities are known the actual E.M.F. of the cell cannot be ascertained. If no current be drawn from the cell, *i.e.*, $C = 0$, then $E = E_v$, so that in order to measure E directly, it will be necessary to adopt a method which does not necessitate the performance of electrical work by the cell. This is effected in the Poggendorf compensation method using the potentiometer.

It might be an advantage here to point out the relationship between the potential difference between the two electrodes of a cell and the E.M.F. of the cell. In " open circuit," *i.e.*, when the two poles are not connected by means of a conducting wire, these effects are equal and opposed to one another, for the current tends to pass from the negative pole through the cell liquid to the positive pole and is urged by the chemical action, *i.e.*, the E.M.F. of the cell, but this transference of electricity is prevented by the difference in potential between that of the positive electrode and that of the negative pole, *i.e.*, P.D. In a " closed circuit " this P.D. becomes smaller than the E.M.F. on account of its forcing the current round the external circuit. The current, C, on attaining a constant value is equal to $\dfrac{P.D.}{R}$ in the external circuit whose resistance is R, whereas this current, C, is equal to $\dfrac{E.M.F. - P.D.}{r}$ when passing through the cell, resistance $= r$. Hence

$$C = \frac{P.D.}{R} = \frac{E.M.F. - P.D.}{r}$$

and therefore,

$$E.M.F. = r \times \frac{P.D.}{R} + P.D.$$

whence

$$E.M.F. = rC + P.D.$$

It will be observed that this equation is identical with the one obtained in the previous paragraph by a somewhat different method.

Poggendorf's Method for the Measurement of E.M.F's.

By this method the electromotive force of a cell is measured by what is equivalent to an " open circuit " method in that no electricity is allowed to flow from the cell while undergoing test.   If we consider the fall in potential produced when a current of electricity is sent along a wire of uniform cross-section and resistance, we find from Ohm's law that the amount of loss in potential suffered by the current is proportional to the length of wire through which it has passed.   Hence if a *constant current* is allowed to pass through such a wire, it is possible to calculate the actual potential difference between two points once the potential difference between any other two points on the wire has been ascertained.   Thus if d_1 be the distance between two points of unknown P.D.$_1$, and d_2 the distance to P.D.$_2$,

$$\frac{\text{P.D.}_1}{\text{P.D.}_2} = \frac{d_1}{d_2},$$

and therefore if either P.D.$_1$ or P.D.$_2$ is known then the other potential difference becomes calculable.   If we connect up a cell, whose E.M.F. it is desired to measure, " in series " with some current indicator, across this wire, *i.e.*, " in parallel " with the potentiometer wire so that the cell circuit makes contact with it at two points d cm. apart, and the potential-fall in both the wire
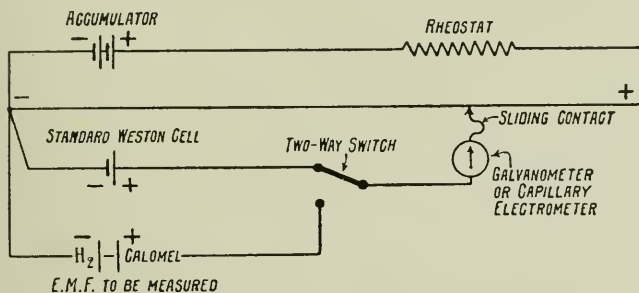
FIG. 17.—Poggendorf's Method for the Measurement of E.M.F.'s.

and the cell take place in the same direction, then it is possible to find some length of wire between the points of contact along which the fall in potential is equal to that acting across the poles of the cell, and as a result it will not be possible for any current to leave the cell as shown by the indicator.   Briefly this is the principle of Poggendorf's method.

Fig. 17 gives the arrangement of the circuit, and the wire

against whose uniform potential gradients other potential dif-
ferences are balanced, is known as the potentiometer. In the
simple metre bridge potentiometer (Fig. 18) this wire is a metre
long, but there is no reason why it should not be any other con-
venient length. In order that there should be a suitable fall in
potential along the wire it should have a resistance of about 10
ohms per metre, but as high resistance is associated with the thin-
ness of the wire care must be exercised not to choose a potential

Fig. 18.—Metre Bridge Potentiometer with Precision Adjustments (Messrs.
Gallenkamp).

wire which is too fine or it may become severely damaged or even
severed by the sliding contact. Wires used for this purpose are
usually made of either manganin (84 per cent. Cu, 4 per cent. Ni,
12 per cent. Mn), German silver (60 per cent Cu, 15 per cent. Ni,
25 per cent. Zn), Eureka (Constantan ; 60 per cent. Cu, 40 per
cent. Ni), or platinoid (German silver + tungsten), and sometimes
platinum or iridio-platinum. The following table, No. 15, gives
the resistances of wires, of different diameters—Standard Wire
Gauge—made of some of these alloys :—

TABLE 15.

RESISTANCE OF WIRE SUITABLE FOR POTENTIOMETERS. (OHMS
PER METRE.)

S.W.G.	Diameter mm.	Manganin.	Constantan (Eureka)	Platinoid.	German Silver.
30	0·315	5·45	6·10	5·25	2·90
32	0·274	7·18	8·04	8·72	3·83
34	0·234	9·90	11·08	9·77	5·27
36	0·193	14·5	12·90	13·99	7·74

The resistance of German silver wire is somewhat too low for
use in potentiometers, and it should be borne in mind that, if the
wire is to be sufficiently durable for general use, it should not be
thinner than 36 S.W.G. and preferably about 32 S.W.G.

The current passed through this potentiometer wire should be
constant and such that the potential difference between the two
ends is about 1·1 volts. For this, a current will be required equal

to $E/R = 1\cdot1/10$ (the resistance of the wire being taken as 10 ohms) $= 0\cdot11$ ampère. If an ordinary accumulator be used as the source of current, and as its resistance is usually negligible, we find that to supply $0\cdot11$ ampère of current the resistance of the complete circuit will have to be $2/0\cdot11$ ohms $= 18$ ohms. Hence an additional resistance of about 8 ohms must be introduced into the accumulator circuit. This is accomplished by including in the circuit either a rheostat (Fig. 17) or simply a suitable length of one of the high resistance wires referred to in Table 15. The required length may be conveniently obtained by allowing one end to pass through a clip connected to the copper wire. The use of comparatively low resistance potentiometers necessitates the flowing of a fairly large current along the wire. As it often is necessary to make a series of E.M.F. measurements at a time, it is an advantage to standardise the potentiometer once for all. This procedure is, however, justifiable only when it is known that the current is being maintained constant. Using low capacity accumulators there is a tendency for their E.M.F's to vary appreciably over protracted periods, and consequently for the currents to change. This can be obviated to a considerable extent by using large capacity accumulators, say of 60 ampère-hours. There is also a risk that currents of this magnitude, in passing through the unknown P.D. circuit whilst the sliding contact is placed at a point on the potentiometer wire such that the two opposing P.D's are not balanced, may disturb the equilibrium prevailing in the cell. Errors from this cause, however, will, in general, be negligibly small, except when the potentiometric system has been kept out of balance for some time. When it is desired to obtain measurements of a higher degree of precision a series of high resistance coils should be substituted for the single wire, as these will permit only extremely small currents to leave the accumulator, though more sensitive galvanometers will have to be employed.

To use the potentiometer to measure E.M.F's it is necessary to set up the apparatus as shown in Fig. 17, in which it will be seen that the negative poles of both the standard Weston cell and the experimental cell are placed in opposition to that of the accumulator. Of course the polarity of all the cells might have been reversed. To standardise the potentiometer the two-way switch is put in the position shown and the sliding contact moved along the wire until no current passes through the indicator—galvanometer or capillary electrometer—shown by no deflection of the former instrument and no movement of the mercury meniscus in the latter. It should be emphasised that contact with the potentiometer wire should be momentary in order that the minimum of

current only might be drawn from the cell. In finding the balance point, it is better to work on both sides of the point and to move the contact inwards until the exact point is found. It is an advantage to have as long a stretch of wire corresponding to the E.M.F. of the Weston cell as possible, seeing the majority of experimental cells have an E.M.F. which fall within the range. This is done by placing the sliding contact in the desired position and adjusting the rheostat in the accumulator circuit. It is now possible to calculate by simple proportion the exact potential gradient in any other length of wire as the E.M.F. of the standard Weston cell is accurately known for any given temperature. Thus at 20° C. the E.M.F. is 1·01830 volts. Hence, if the determinations are being carried out at 20° C. and the potentiometer is a little longer than a metre, it will facilitate calculation of unknown E.M.F's if the potential gradient in 101·83 cm. of wire is made equal to 1·0183 volts, the E.M.F. of the standard Weston cell. Then 1 cm. of wire will correspond to 0·01 volt and 1 mm. to 0·001 volt. Slide wire potentiometers are constructed with vernier scales affixed to the sliding contact which permit of measurements being made accurately to one-tenth of mm., and therefore under the above conditions to 0·0001 volt. The potentiometer illustrated in Fig. 18 sold by Messrs. Gallenkamp has such a provision. To measure the E.M.F. of the experimental cell its circuit must be closed by throwing over the two-way switch and the position of the sliding contact found which causes no current as indicated by the null-point instrument. Its E.M.F. can then be read off directly from the bridge reading, or if the potentiometer has not been standardised in this particular manner, then

$$\frac{\text{E.M.F. of experimental cell}}{\text{E.M.F. of Weston cell}} = \frac{d_e}{d_w}$$

where d_e = length of wire whose potential gradient is equal to the E.M.F. of the experimental cell, and

d_w = length of wire whose potential gradient is equal to the known E.M.F. of the Weston cell.

As before mentioned this relationship presupposes that the potentiometer wire is of uniform gauge, and consequently before using a potentiometer for precision work, the wire should be calibrated. This may be done by means of resistance boxes arranged to form a Wheatstone's bridge, or by the method of Strouhal and Barus. (For details, see Ostwald-Luther, *Physiko-Chemische Messungen*, 4th edition, 1925, pp. 434-440.) Care must be always taken to see that the sliding contact is kept in a satisfactory state and does

not become corroded, which may be prevented by covering it with a very thin film of pure vaseline.

It is often more convenient to use a potentiometer in which the complete circuit is enclosed in a box, and in which the slide wire is replaced by a series of accurately constructed resistance coils made to correspond to P.D's of, say, from 0 to 1·7 volts and a slide wire wound on a revolving drum which is subdivided so that the smallest divisions may be made to correspond to 0·0001 or 0·0002 volt.   Fig. 19 is a picture of the Cambridge potentio-
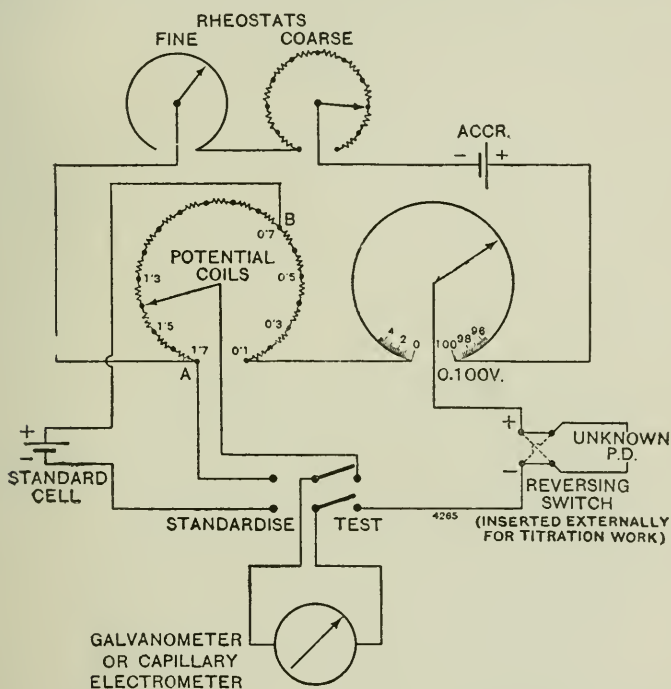
FIG. 20.—Schematic Diagram of a Circuit of the Cambridge Potentiometer.

meter, and Fig. 20 a simple schematic diagram of its circuit, which the author has found to be admirably suited to hydrogen-ion work.   All its moving parts, with the exception of the handles of the controlling switches, are inside the case, thus eliminating corrosion and other deteriorating effects.   It has a selective switch and terminals which enable three different experimental cells to be connected to the potentiometer at the same time.   The remaining terminals connect to the galvanometer or capillary electrometer, the standard Weston cell and the accumulator

respectively. Thermo-electric effects are reduced to a minimum by having the resistances made of manganin and hard soldered to copper. To standardise the instrument, it is necessary to depress the standardising key provided, thereby throwing the standard cell into circuit with the null-point indicator and at the same time breaking the experimental cell circuit, and to adjust the rheostats (coarse and fine) until the flowing of no current is indicated. By so doing the figures given on the two potentiometer dials refer to volts, and consequently by rotating these dials until the null-point is obtained on depressing the tapping-key. The standardising key and the rheostats may be adjusted at any time thus enabling the potentiometer to give accurate readings.

The Cambridge Instrument Co. produces an excellent portable potentiometer, which can be standardised without a standard cell. It is specially adaptable to hydrogen-ion concentration determinations and is capable of giving voltages correct to 1 millivolt, which happens to be the limit of accuracy to be expected from the hydrogen electrode unless extreme precautions be taken, and, moreover, a sufficiently delicate electrode be employed. It contains a galvanometer of the unipivot type, which is used both in connexion with the standardisation of the instrument and as the null-point indicator. Fig. 21 is a picture of the Cambridge instrument. The instrument also contains an adjustable resistance to standardise the battery circuit with the galvanometer, a five-range switch to give steps of 200 millivolts and a fine adjustable resistance. The electrodes are connected to the right-hand terminals of the instrument, a dry cell being connected to the left-hand terminals. With the standardising key depressed, the rheostat is adjusted until the pointer of the galvanometer is directly over the red mark on the scale. The " X " key is then lightly depressed and the range switch set to give the minimum deflection while the circular graduated dial is at zero. To obtain the final reading the latter is rotated until the pointer comes to zero. The reading of the circular dial is then added directly to the number of millivolts indicated by the range switch, this total giving the E.M.F. of the electrodes.

We shall now direct our attention to the several components included in the potentiometric system.

The Experimental Cell Combination.

Fig. 22 represents the simplest cell arrangement involving the hydrogen and calomel electrodes, and contact with each electrode
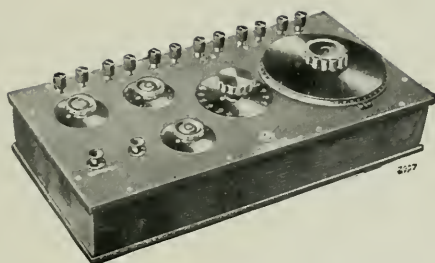
Fig. 19.—Cambridge Slide Wire Potentiometer
(Cambridge Instrument Co., Ltd.).

[*See page* 107.

Fig. 21.—Cambridge Portable Potentiometer.

[*To face page* 108.

is made by means of amalgamated copper wire dipping into mercury. As stated on page 20 the potential difference at the junction of the liquids in the two electrodes can, for all practical purposes, be eliminated by inserting a saturated solution of potassium chloride between them. The narrow glass cylinder is filled with this solution to the level of the liquid in the beaker.
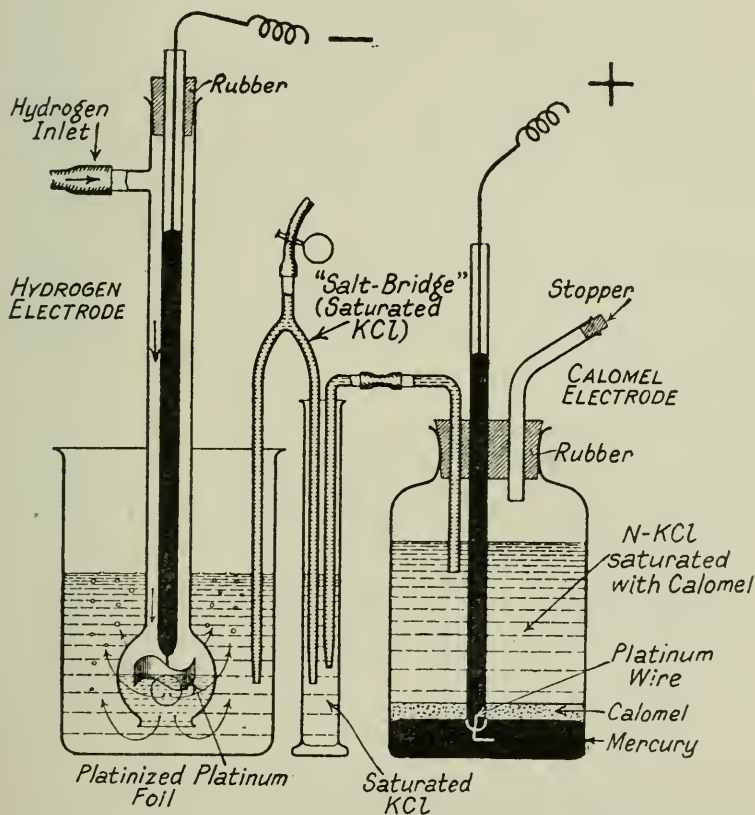
FIG. 22.—Hydrogen Electrode Titration Apparatus.

These two solutions are connected through the " salt bridge," a narrow inverted U-tube, containing saturated KCl solution. This " salt bridge " tube should not be made of capillary tubing as this would create a new source of potential. It is filled by suction with saturated potassium chloride solution by inserting both ends in a beaker containing the solution. If the hydrogen electrode should be contained in a closed vessel, then this " salt bridge " is dispensed

with, and the connecting arm of the hydrogen electrode simply dipped into the vessel of saturated potassium chloride solution. A difficulty which sometimes arises is perhaps worthy of note. It may occur that a bubble of air settles over the orifice of one of the connecting tubes, which thereby breaks the circuit, but often evades observation. In carrying out an electrometric titration care has to be taken to keep the level of the solution in the cylinder the same as that in the beaker. This is omitted by some workers, who either insert filter paper impregnated with KCl in the two ends of the U-tube to prevent diffusion, or fill the tube with agar containing saturated KCl solution. The use of filter paper, however, tends to give poor contact, with a consequent sluggishness in the attainment of the equilibrium E.M.F's.

The junction liquid may also be inserted in one half of the tube leading from the calomel cell, through a funnel and a three-way tap fitted in the tube. Such a device is shown in Fig. 31, and thus permits the end of the calomel connecting arm to dip into the solution. This arrangement is more suitable with the saturated calomel electrode and is particularly useful for rapid electrometric titrations.
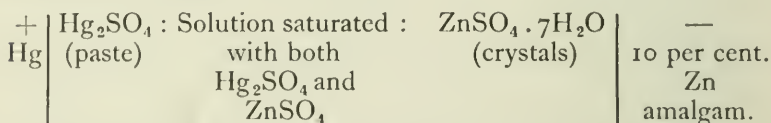
The Standard Cell.

Two standard cells are available, namely (a) the standard Weston cell, and (b) the Clark cell. Schematically, they may be represented thus :

Standard Weston :

+	Hg_2SO_4 :	Solution saturated	: $3CdSO_4 . 8H_2O$	—
Hg	(paste)	with both	(crystals)	12·5 per cent.
		Hg_2SO_4 and		Cd
		$CdSO_4$		amalgam.

Standard Clark :

+	Hg_2SO_4 :	Solution saturated :	$ZnSO_4 . 7H_2O$	—
Hg	(paste)	with both	(crystals)	10 per cent.
		Hg_2SO_4 and		Zn
		$ZnSO_4$		amalgam.
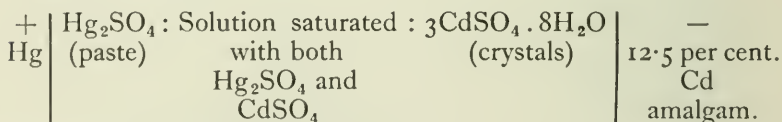
In terms of international units, the standard Weston cell has an E.M.F. of 1·01830 volts at 20° C., and according to Wolff (1908) its E.M.F. at any other temperature, $t°$, between 0° to 40° C. may be found from

$$E_t = E_{20} - 0.0000406(t - 20) - 9.5 \times 10^{-7} (t - 20)^2.$$

The E.M.F's at different temperatures are given in Table 16 :—

TABLE 16.

E.M.F. OF STANDARD WESTON CELL AT VARIOUS TEMPERATURES.

Temp. °C. E.M.F.	0°. 1·01866.	10°. 1·01860.	15°. 1·01848.
Temp. °C. E.M.F.	20°. 1·01830.	25°. 1·01807.	30°. 1·01781.

The Clark cell might be considered obsolescent, and unlike the Weston cell it has a large temperature coefficient, as shown by the following formula which gives its E.M.F. between 10° and 25° C. :—

$$E_t = E_{15} - 0.00119(t - 15) - 0.000007\,(t - 15)^2,$$

the E.M.F. at 15° C. (E_{15}) being 1·4326 international volts.

The small temperature coefficient of the Weston standard cell was found by Smith (1910) to be due to the positive electrode increasing by 0·00031 volt per degree rise in temperature at 20°, whereas the negative pole undergoes a diminution of 0·00035 volt. For this reason it is advisable to protect the cell from local heating by enclosing it in a suitable container.   Fig. 23 shows a convenient method of mounting the cell, which is enclosed in a brass cylindrical box.   Sometimes two Weston cells are mounted side by side in order that one may be compared against the other.   It is an advantage to have a hole in the ebonite top through which a thermometer may be inserted.   These cells are now supplied with, if so desired, a certificate of the exact E.M.F., issued by some public testing institute, *e.g.*, by the National Physical Laboratory in England, or by the Bureau of Standards in the U.S.A., or by the Physik.-Techn. Reichanstalt in Germany.

In laboratories where many E.M.F. determinations have to be made, it is advisable to retain the standard cell which has been checked against a cell of accurately known E.M.F. as a standard, and to prepare a working cell.   These may be readily prepared in the following way.   A H-shaped vessel, similar to that illustrated in Fig. 24 is procured, and in the closed ends are carefully fused two short pieces of platinum wire.   Into one limb is placed a little pure mercury and into the other a little cadmium amalgam. This amalgam should contain 12·5 per cent. (by weight) of pure cadmium (it must be free from zinc).   It is prepared by mixing the

two metals, warming on a water-bath and stirring the resulting
liquid amalgam until it has become thoroughly homogeneous.
Should any cadmium oxide be formed it must be removed, and
this may be effected by passing the molten amalgam through a
test-tube, the end of which has been drawn out into a long capillary.
It is then poured into the bottom of one side of H-tube and to
prevent fracture of the glass tube by the hot amalgam, the tube
should be kept in suitably hot water. On removing from water
the amalgam solidifies. This amalgam is covered with a thin
layer of finely-powdered crystals of cadmium sulphate and then
with large crystals to keep the cadmium sulphate solution satu-
rated. A saturated solution of cadmium sulphate is prepared
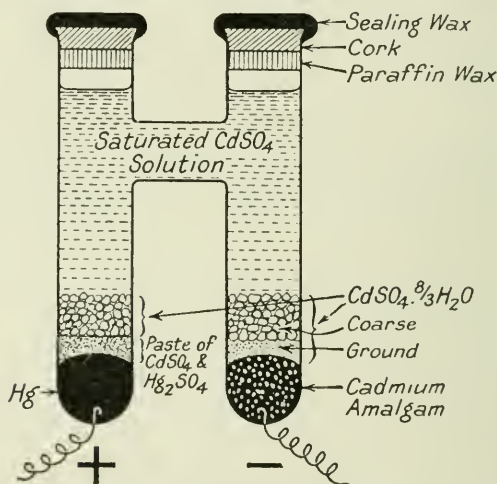
Fig. 24.—Weston Standard Cell.

from the crystals, $3CdSO_4$, $8H_2O$, and if heating is resorted to it
should be as gentle as possible and on no account should the
temperature be allowed to rise above $75°$ C., for at this temperature
the stable solid phase is $CdSO_4$, H_2O, and this will influence the
concentration of the liquid phase. Moreover, hydrolysis of salts,
such as would occur at elevated temperatures, is known to have
an effect upon the amount of cadmium sulphate required to satu-
rate a solution at any given temperature. The paste of mercurous
sulphate is made by rubbing the pure salt with mercury and a
little of the cadmium sulphate solution together in a mortar,
filtering through a funnel plugged with cotton wool to remove
any mercuric sulphate, and repeating the process two or three
times with fresh quantities of mercury and cadmium sulphate

solution.   This paste is placed on top of the mercury, covered with crystals of cadmium sulphate and the vessel nearly filled with the saturated cadmium sulphate solution.   The vessel is sealed in the manner indicated in Fig. 24.   The E.M.F. of the cell should be tested from time to time by comparison with a standardised Weston cell.   Some kind of support will be necessary, *e.g.*, a large cork having two holes in which the two limbs fit.

Null-Point Indicators.

Quadrant electrometers are never used in conjunction with the hydrogen- or hydrogen-functioning electrodes, except in the case of the glass electrode.   The capillary electrometer, Fig. 25, being the modified form of Ostwald and Luther, may be used, or suitable types of moving coil galvanometers which are rapidly coming into favour.

Capillary Electrometer.

This instrument, which in the first place was due to Lippmann (1873), depends upon the fact that there exists a difference in potential between a metal and a solution, which affects the surface energies of the two substances at the interface.   If, therefore, it happens that the metal is a liquid, *e.g.*, mercury, then we see that its surface tension at the interface must be governed by the potential difference prevailing across the interface.   Thus the potential difference between mercury and dilute sulphuric acid (1 part in 6 of water) is 0·93 volt.   Hence, if an external positive potential be applied to the mercury, its surface tension will decrease such that if the mercury-acid interface occurs inside a capillary tube, this diminished surface tension will result in the mercury meniscus rising higher up the tube.   On the other hand, if a current is made to flow across the interface from the acid to the mercury the potential of the mercury will become less positive, and this, in increasing the surface tension of the mercury, will cause the level of the mercury to become lower in the capillary.   In the electrometer shown in Fig. 25 this interface is arranged to be about mid-way up the capillary tube in the middle, and the dilute sulphuric acid which lies upon it connects it to the mercury in the bulb on the right.   Platinum wire contacts are sealed through the apparatus in the positions indicated.   On joining up these two contacts with a copper wire the mercury-acid interface acquires its normal contact potential and the meniscus almost immediately assumes its original condition.   The movement of the mercury level on momentarily passing a current through the electrometer

8

can be seen through a microscope fitted directly in front, Fig. 26, and illuminated, if necessary, by a suitable electric lamp placed immediately behind. With satisfactory magnification the minutest movement can be detected. Observation is facilitated by including a vertical scale in the eyepiece. It must be borne in mind that
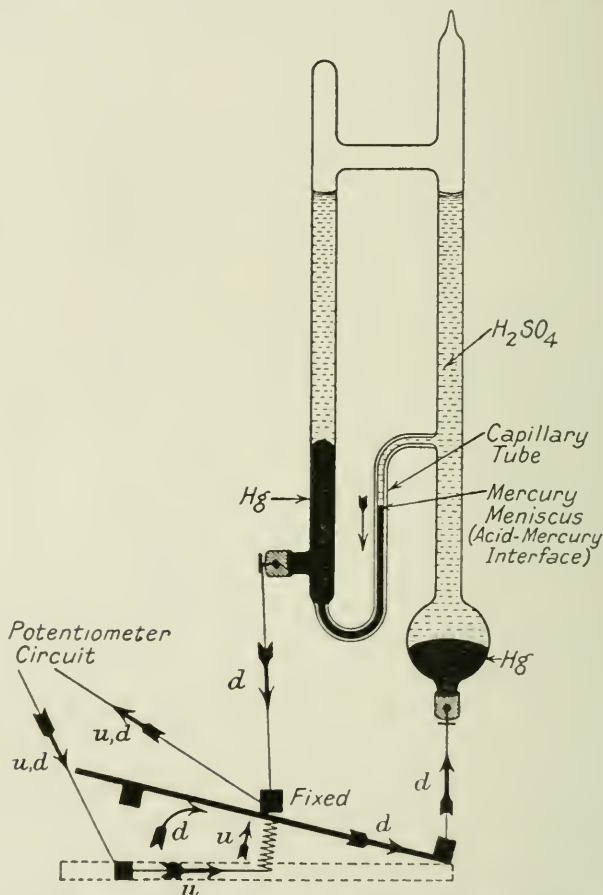

FIG. 25.—Capillary Electrometer showing Short-circuiting.

the current passed through the electrometer must, at most, be only for a few moments, and instantaneous when large currents are indicated. The reason is that electrolysis will ensue, and should the current flow across from the mercury across the interface to the acid solution, it is possible the mercurous sulphate may be deposited on the wall of the capillary and so tend to clog it up.

Hence, it is necessary to short-circuit the electrometer so as to allow current to pass through only for the very brief periods when making a reading. This is accomplished by means of a tapping key, Fig. 27, and which is diagramatically explained in Fig. 25. The letter u indicates the direction of the current from and to the potentiometer when the tapping key remains up, the position shown, and d the direction when the key is depressed. In the former case the current passes through the spring and back to the potentiometer, and in the latter, after passing through the spring it is conducted through the key arm into the electrometer and from thence to the potentiometer. For the reason stated above it is preferable to search for the null-point with the current flowing in this direction, though, of course, contact will have occasionally to be made so that the current flows through the electrometer in the reverse direction, in fact, very often the only way to find the null-point is to make contact on each side of the balance-point and to work inwards until the point which gives no movement of the meniscus is found. This electrometer has the advantage that it is dead-beat, and on short-circuiting the meniscus passes back immedi-

FIG. 26.—Complete Capillary Electrometer Outfit.

ately to the zero level. The form shown in Fig. 25 is especially serviceable in that, should the capillary have become impaired through the deposition of mercurous sulphate, it can easily be cleaned by inverting the electrometer, allowing the mercury to flow through the capillary, and exposing a new meniscus to the acid.
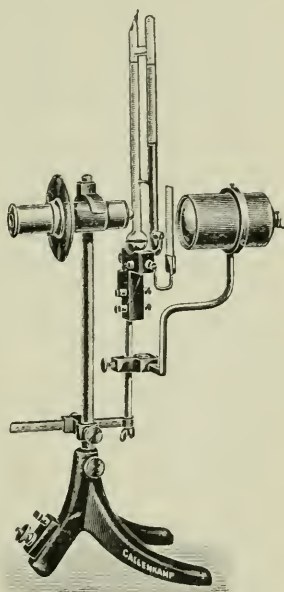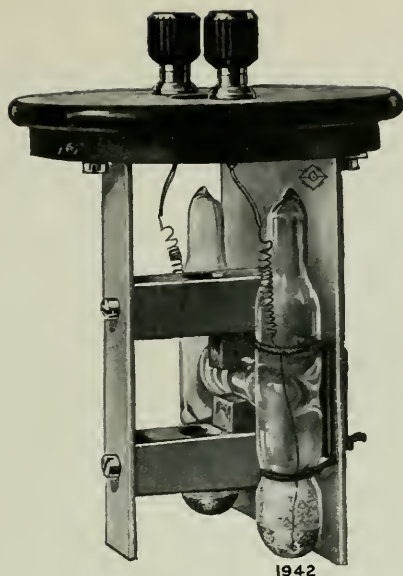
Galvanometers.

Galvanometers are becoming more popular in electrometric determinations, though in order to get the necessary sensitivity the D'Arsonval moving coil pattern must be chosen. With such a type it is more usual to have a mirror attached to the moving coil, which moves between the poles of a strong permanent magnet, and to observe the movement of a reflected spot of light upon a

distant scale. This is a disadvantage, which coupled with the fact that such a galvanometer often requires some time to respond completely to slight currents, probably explain why the capillary electrode is still preferred by many workers. In recent years, more attention has been directed to the production of more satisfactory galvanometers. Thus the unipivot type of moving coil galvanometer included in the Cambridge portable potentiometer (Fig. 21) is extremely useful and satisfactory in every way, so also for routine work is the self-contained Daylight Reflecting Moving-coil Galvanometer, manufactured by Messrs. Philip Harris & Co., Ltd., of Birmingham, and illustrated in Fig. 28. This particular instrument is fitted with the " Harris " system of coil arrestment, and is supported upon a baseboard together with a 2-volt lamp, which when connected to a suitable battery, a beam of light is reflected upon a special mirror fitted to the moving coil and received upon a scale 90 mm. long with central zero mounted upon a ground glass window. This galvanometer may be used in daylight and is dead-beat. It has a resistance of 150 ohms and gives approximately 10 divisions deflection per micro-ampère. Most scientific instrument makers have now available galvanometers suitable for hydrogen-ion work, and when a galvanometer is to be purchased some points to be remembered are that (i) it must be responsive to momentary currents, for contact should not be made with the potentiometer wire for more than about ten seconds at a time ; (ii) it should have sufficient sensitivity, but not too much, for the work it is intended ; and in this connexion it is advisable to calculate the minimum currents to which it must respond—these will be smaller in testing experimental cells of high resistance ; and (iii) it should be possible to damp its vibration rapidly. For great precision a much more sensitive galvanometer must be used than the one described above.

Fig. 23.—Internal View of " Cambridge " Weston Standard Cell.
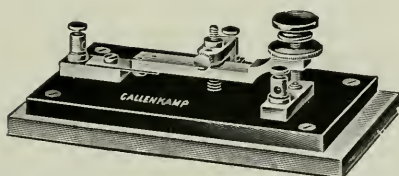
Fig. 27.—Tapping Key for " Short-Circuiting " Capillary Electrometer.
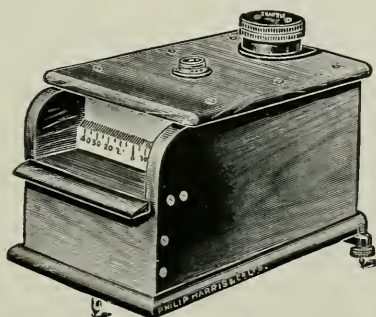
Fig. 28.—Daylight Reflecting Moving-Coil Galvanometer (Messrs. Philip Harris & Co., Ltd., Birmingham).

CHAPTER IX.

MODIFIED POTENTIOMETRIC METHODS.

THE simple method of determining potential differences by means of the potentiometer may be modified in the following ways :—

- (*a*) By using two precision decade resistance boxes ;
- (*b*) By placing a voltmeter across a resistance between the ends of which the fall in potential is made equal to that of the unknown potential difference, and
- (*c*) By using a thermionic valve.

These methods will now be discussed.

Decade Resistance Box Method.

This method has the advantage, if two accurate decade resistance boxes are available, that the current drawn from the accumulator can be made as small as desired which will assist the accumulator to maintain a constant current, and will prevent large currents from being extracted from the cell under test that otherwise would destroy the cell equilibria. The circuit is arranged in the usual potentiometer system, as given in Fig. 29, in which the two resistances, placed in series, take the place of the potential wire, and the side circuits are connected across one of the boxes only. To establish a constant current in the accumulator circuit, resistance

FIG. 29.—Potentiometric System, using Two Precision Resistance Boxes.

is introduced equal to some definite number of ohms, say 100, 1000 or 10,000 ohms, by removing plugs from either of the boxes.
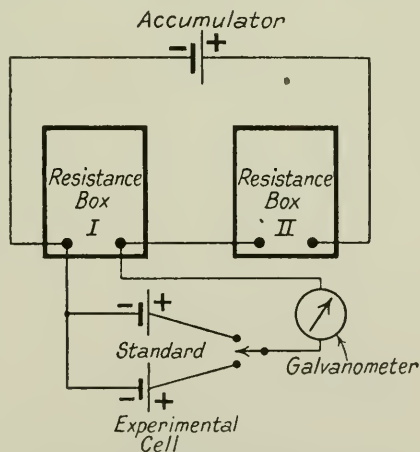
Then the resistance plugs are taken from Box I required to balance the side circuit, as shown by galvanometer, and whatever plugs are taken from one box are placed in the corresponding sockets in Box II so as to keep the constant resistance in the accumulator circuit. Thus, if x ohms resistance were required to be used in Box I, and it was arranged to keep a total resistance of 1000 ohms from Boxes I and II together, then

$$\text{E.M.F. of experimental cell} = \frac{x}{1000} \times \text{P.D. across 1000 } \Omega.$$

The P.D. between the ends of the 1000 ohms resistance must be found in the usual manner with the standard Weston cell.

This method is essentially that using the Ostwald " Decade " Rheostat, by which the accumulator is connected across 1000 ohms and the side circuit connected across the resistances required to give balance by means of two wander plugs. (For further details, see Ostwald-Luther, *Physiko-Chemische Messungen*, 4th edition, 1925, p. 463.) Needless to add, in employing a resistance box method every care must be taken to see that all plugs are fitting exactly.

Potentiometer–Voltmeter Method.

In this method full dependence is put upon the voltmeter with which the potential measurements are made. Instead of using a potentiometer wire the accumulator is connected across a suitable rheostat, and the side circuit connected from one end to the sliding contact, in parallel with which is a voltmeter. When the sliding contact has been moved to the position which indicates that no current is passing through the galvanometer, the potential difference corresponding to that of the test-cell is read off from the voltmeter. Such a method was used in conjunction with hydrogen electrode measurements by Sand and Law (*J. Soc. Chem. Ind.*, 1911, **30,** 3872) and later by Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35,** 847). Figs. 30 and 31 are of the electrometric titration apparatus manufactured by Messrs. A. Gallenkamp & Co., of London. The principle underlying the method of measuring the E.M.F's is that described above, but in order to get an exact balance of potential two rheostats are employed, one for coarse adjustment and the other for fine adjustment. It will be observed, Fig. 31, that the accumulator (in this set a dry battery is provided) is connected across the two resistances R and R_1, and the potential difference of the cell under test is made equal to the fall in potential along a portion of these rheostats

between the two points of contact by moving the sliding contacts RC and RC₁ until no deflection is obtained in the galvanometer. When this state of affairs is established, the P.D. is observed on the voltmeter. In using this compact piece of apparatus, it is unnecessary to keep the battery switch, BS, closed except when taking a measurement. Kling and M. and Mme. Lassieur (*Comp.*
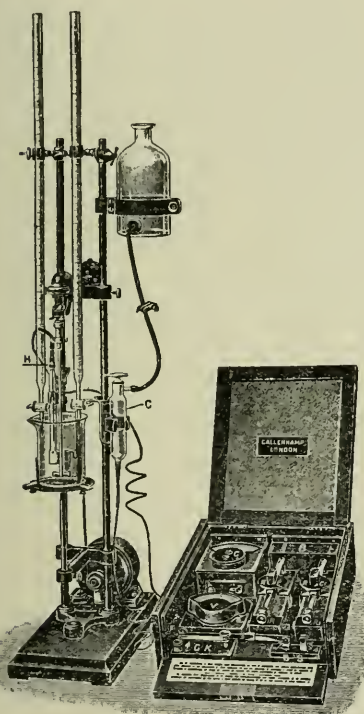

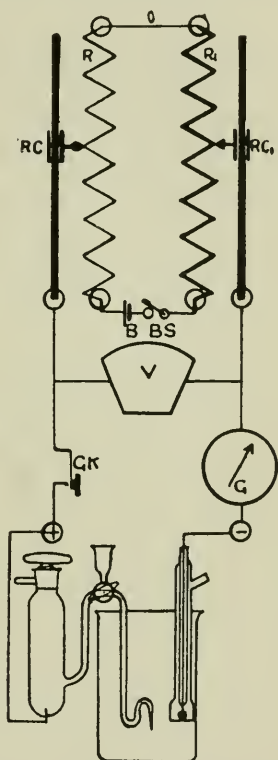FIG. 30.—Electrometric Titration Apparatus (Messrs. Gallenkamp).

FIG. 31.—Circuit Diagram of Electrometric Titration Apparatus (Messrs. Gallenkamp).

rend., 1922, **174,** 165) have described a similar circuit in which they use a millivoltmeter and also two movable contacts, one moving along a rheostat of 195 ohms, whereas the other is used for fine adjustment and moves upon a resistance of 5 ohms.

This method is convenient for titration work and has the distinct advantage that neither is a standard cell, nor are accurate resistances required. One difficulty encountered, however, apart

from the fact that the voltmeter will require periodical checking, is that a voltmeter which covers the whole range of E.M.F's met with in titration work usually reads only to 1 centivolt, and consequently reading to a millivolt will be approximate.

Thermionic Valve Method.

As mentioned before in this chapter that in making E.M.F. measurements of cells, of which one electrode is that of hydrogen, every precaution must be taken not to draw any more current from the experimental cell than is absolutely unavoidable on account of the risk of upsetting the equilibrium existing between that electrode and the solution in which it is immersed. It is, moreover, essential that the sliding contact should complete the test-cell circuit with the potentiometer only for those short periods when observations are being made. By means of the thermionic valve it is possible to make observations without extracting from the cell any appreciable amount of current, and for this reason it is possible to perform electrometric titrations with the hydrogen electrode whilst leaving the titration-cell in circuit. Goode (*J. Amer. Chem. Soc.*, 1922, **44,** 26) first applied the valve to electrometric titrations with the hydrogen electrode. In the ordinary triode valve the plate or anode is maintained at some high positive potential, the grid is given a negative potential, and the filament made incandescent by means of a suitable low potential. In so doing, it emits a stream of electrons, which though repelled by the grid, are attracted to the positive plate. Thus a current of negative electricity is generated in the anode circuit away from the anode, or, conversely and, incidentally, according to the more usual convention, a current of positive electricity flows from the plate through the valve to the positive filament-lead into the anode circuit. Goode pointed out that this *plate or anode current* might be considered as the sum of a constant current, which depends upon the valve and its applied potentials only, and the remaining portion which, besides being dependent upon the negative grid potential, is a linear function of the potential applied to the grid. Hence, when no potential is applied to the grid, the plate current depends entirely upon the valve, and if some equal opposing current can be introduced into the anode circuit, it should be possible to neutralise the current set up by the valve alone, so that when some negative potential is applied to the grid the current, generated in the plate circuit, will be a linear function of that potential. This Goode accomplished with the circuit represented in Fig. 32. The hydrogen electrode, being the negative pole of the titration cell,

was connected to the grid and the calomel electrode to the negative filament lead. A shunted (S) moving coil galvanometer, G, detected currents in the anode circuit, and the anode current due to valve with no cell in the grid circuit was opposed by an equal current passing through the galvanometer, produced by a potential difference between the two ends of a small resistance placed in the positive filament lead, and regulated by means of a large variable resistance, VR. Thus, having once adjusted the galvanometer circuit such that no current flows through it when there is no applied grid potential, the current registered by the galvanometer when the titration cell is introduced into the grid circuit will bear some simple proportional relationship to its E.M.F. The galvanometer may, therefore, be calibrated in terms of the applied
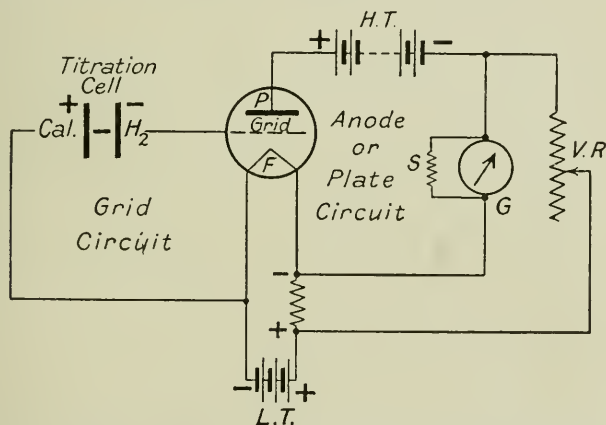

FIG. 32.—Goode's Thermionic Valve Electrometric Titration Circuit.

voltages, or simply in terms of pH. Hence if an electrometric titration be performed, a curve will be obtained between the amounts of reactant added and galvanometer readings which will be similar in form to that obtained by direct titration. Later, Goode (*J. Amer. Chem. Soc.*, 1925, **47,** 2483) described a circuit by which the original plate current was amplified about 25 times, by two stages of valve amplification using resistances, and thereby he was able to read off the pH values from a milliammeter after suitable calibration. Treadwell (*Helv. Chim. Acta*, 1925, **8,** 89) used a similar arrangement for electrometric titration with the exception that he placed an additional potential of 1·6 volts in the grid lead between the negative electrode of titration cell and the grid.

Morton (*Pharm. J.*, 1927, **118,** 761) has recently modified Goode's procedure, and has shown that not only is it possible to
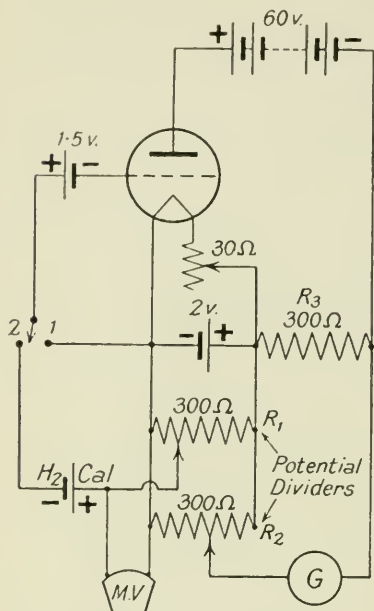
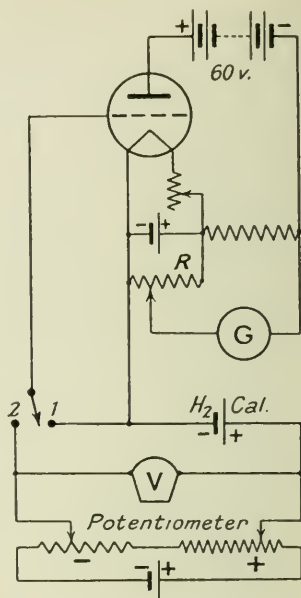FIG. 33.—Morton's Differential Method
of Electrometric Titration.

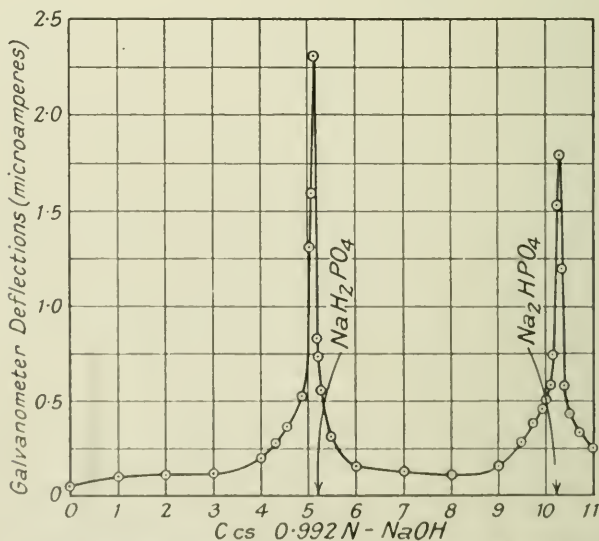FIG. 35.—Galvanometer in Anode
Circuit to Balance Potentio-
meter.

FIG. 34.—Differential Titration Curve of 5 c.c. 1·022 M—H₃PO₄ with
0·992 N—NaOH.

measure the voltages set up by a titration cell, but to locate the
end-points more accurately than is possible from the ordinary
titration curve.   This is done by means of a differential curve
which is obtained by plotting the amount of reactant added against
the increase in the deflection of the galvanometer for each increment
of titrant.   This is obtained by balancing out the component of
the normal anode current as described above, then including the
titration cell in the grid-filament circuit and again causing the gal-
vanometer in the anode circuit to remain undeflected.   After-
wards small amounts of reactant are added, each galvanometer
deflection observed, and the potential dividers adjusted after
each addition so as to give no galvanometer deflection.   The
galvanometer readings thus obtained are proportional to $\frac{dE}{dx}$, where
E is the E.M.F. of the titration cell when x c.c. of reactant have
been added.   Fig. 33 gives the arrangement of Morton's circuit.
The method is to place the switch in position 1 and then to balance
out the anode current by adjusting R_2.   Throw switch over to
position 2, thereby including titration cell in the grid-filament
circuit and now adjust R_1 until the galvanometer again remains
undeflected.   An increment of reagent is added, the galvanometer
reading noted, and again balanced out, and so on.   Fig. 34 gives
a curve obtained by this method in which it will be seen that the
end-points, corresponding to points of inflection (*cf*. Fig. 41) were
marked maximum galvanometer readings.   The ordinary titration
curve can be drawn from observations of the millivoltmeter, MV.
Morton (see also Crocker and Matthews, *Theoretical and Experi-
mental Physical Chemistry*, London, 1927, p. 412) showed that the
valve-galvanometer circuit could be used for ascertaining the point
of balance of a potentiometric system when connected across from
the grid to the negative-lead to the filament, in such a way that the
negative potential is joined to the grid (Fig. 35).   The anode
current produced when the switch is in position 1 is balanced out
as above by adjustment of R, and when the switch is moved to
position 2, the sliding potentiometer contacts are adjusted until
the galvanometer remains undeflected.   The potentiometer is
then balanced, and the potential may be read off from the poten-
tiometer as usual or in Fig. 35 from the voltmeter.   (See also
Buytendijk and Brinkman, *Proc. K. Akad. Wetensch., Amsterdam*,
1926, **29**, 816.)

CHAPTER X.

THE PRINCIPLES OF VOLUMETRIC ANALYSIS.

The Importance of Electrometric Titration.

VARIATIONS in hydrogen-ion concentration, or may be " hydrogen-ion activity," underlie many analytical procedures. This has become apparent from the results of the enhanced attention which has been devoted in recent years to the neutralisation reactions of acids, bases, and ampholytes, which include many protein bodies and alkaloids. Besides leading to a clearer understanding of the principles of analysis, they have, moreover, led to the discovery of new methods for the estimation of these acids and bases which are too weak to be titrated volumetrically in the usual way with the aid of indicators.

In this chapter the aim will be to give a survey of the subject in so far as it concerns volumetric analytical practice, and in so doing to emphasise the practical bearing and significance of the physico-chemical affinity constants of acids and bases. The importance of these constants is apt to be regarded as being merely theoretical, instead of providing, as they do, a measure of the reactivity, and in this respect they may be truly said to supply the only real information relating to acids and bases. It is therefore surprising to find that often in the teaching of both inorganic and organic chemistry very little attention is directed to the fact that many reactions are the direct outcome of the magnitude of certain physical chemical constants. This is largely due to the artificial, though convenient, isolation of physical chemistry from the other sections of modern chemistry curricula.

Practical Significance of the Dissociation Constants of Acids and Bases.

It is feared that much of the failure to appreciate the full practical meaning of dissociation constants lies in the apparent complexity of the constants themselves, it being difficult to grasp the real significance of constants of such small magnitudes, as say, 10^{-5} or 10^{-13}. The development of the idea of representing varying

degrees of acidity and alkalinity in terms of concentrations of hydrogen-ions, or more simply in terms of pH, has supplied a means by which dissociation constants, however small they may be, become intelligible, so much so that it is an easy matter to find what variations in pH which any particular acid or base will set up whilst undergoing neutralisation.

The equilibrium constants governing the ionisation of an acid, thus $HR \rightleftharpoons H^{\cdot} + R'$, or a base, thus
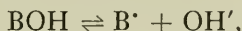
$$BOH \rightleftharpoons B^{\cdot} + OH',$$

may be expressed as

$$K_a = \frac{[H^{\cdot}][R']}{[HR]}, \text{ and } K_b = \frac{[B^{\cdot}][OH']}{[BOH]}$$

respectively, where the quantities enclosed in square brackets represent the concentrations of ions or of undissociated acid or base denoted. If the acid or base be dissociated to the extent of a fraction, α, of the concentration, C, present, then the concentrations of each of the various ions will be αC, and the concentrations of undissociated acid or base will be $C - \alpha C$, or $(1 - \alpha)C$, and therefore K_a or K_b will be equal to

$$\frac{\alpha C \times \alpha C}{(1 - \alpha)C} = \frac{\alpha^2 C}{1 - \alpha}.$$

This expression is satisfied by acids and bases which give constants of 10^{-3} and less. The extent to which dissociation proceeds in solutions of concentration, of say, M/100, of either the free acids or bases whose constants decrease from 10^{-3}, have been calculated and are given below :—

TABLE 17.

SHOWING VARIATION IN THE VALUES OF α FOR M/100 SOLUTIONS OF ACIDS AND BASES WITH DIMINISHING K_a OR K_b.

K_a or K_b	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}
α	0·270	0·095	0·031	0·010	0·003	0·001

It will be seen that when K_a or K_b has become so low as 10^{-6} the value of α becomes equal to 1 per cent. When, however, the free acid or base is partially neutralised by a strong base, e.g.,

NaOH, or a strong acid, *e.g.*, HCl, as the case may be, the value of α rapidly becomes diminished through the formation of salts and the consequent introduction of appreciable concentrations of common ions, anions in the former case and of cations in the latter case. Thus, consider the reactions (1) $HR + NaOH = NaR + H_2O$ and (2) $BOH + HCl = BCl + H_2O$, which, when they take place in dilute solutions will produce (1) NaR and (2) BCl, which, for all practical purposes, may be considered to ionise completely to give equivalent concentrations of R′ and B˙ respectively. The relatively large concentrations of ions so produced drive back the ionisation of the free acid, and they may become so large as to prevent the ionisation of the acid altogether, or more accurately stated to reduce the ionisation to within almost infinitesimal limits. Hence, the expression

$$K_a = \frac{[H˙][R′]}{[HR]}$$

might then be rewritten

$$K_a = [H˙] \times \frac{[salt]}{[acid]}$$

in order to represent the variation in hydrogen-ion concentration throughout a neutralisation reaction in which the concentration of R′-ions from the salt formed is sufficient to depress to within negligible limits the dissociation of the unneutralised acid. If x is the number of c.c. of strong alkali required for neutralisation, and y the number of c.c. of alkali actually added, then the hydrogen-ion concentration may be calculated from

$$K_a = [H˙] \times \frac{y}{x - y}$$

and similarly from

$$K_b = [OH′] \times \frac{y}{x - y}$$

for bases. Fig. 36 gives a graphical representation of the variation in pH during the neutralisation of acids and bases having different constants. The hydrogen-ion concentrations were calculated from these expressions for the curves corresponding to K_a 10^{-4} to 10^{-10} and K_b 10^{-4} to 10^{-10}, except for the beginning of the neutralisation reactions before the concentrations of the suppressing ions had grown sufficiently large to have their maximum effect on α. Here α had to be taken into account, and in order to arrive at specific values of hydrogen-ion concentration the initial concentration of acid or base was taken as centimolar. The shaded

portions show the divergence from the curve so found and the curve corresponding to the above expression. For acids of K_a greater than 10^{-4} the magnitude of α is too great to be without effect and the curves vary with the dilution. Thus, two curves are given which show the courses of neutralisation of M/10 and
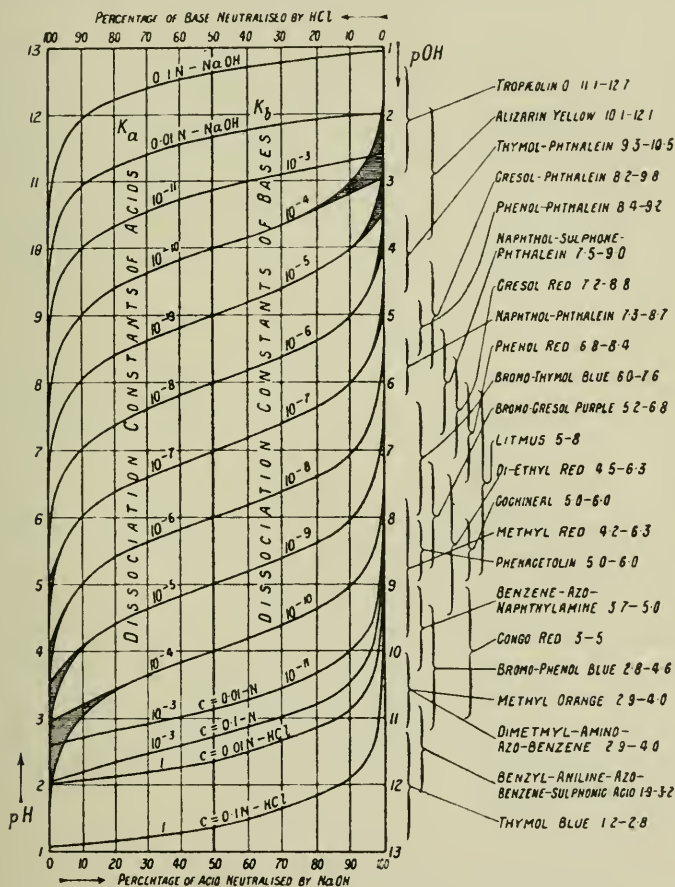
FIG. 36.—Variation in pH during Neutralisation of Acids and Bases.

M/100 acid solutions of $K_a = 10^{-3}$. The two bottom curves refer to the neutralisation of M/100 and M/10 — HCl solutions with NaOH. The curves of acids having constants greater than 10^{-4} lie in the lower section of the diagram. If a temperature, namely, $22°$ C., be taken such that K_w, the ionic product of water, is exactly 10^{-14}, then the neutralisation curves of the bases, of

which $K_b = 10^{-x}$, with hydrochloric acid, will be coincident with those of acids $K_a = 10^{-(14-x)}$, *when the amount of neutralisation is plotted in the reverse order as shown by the abscissa at the top of the diagram.* During the second half of the neutralisation of weak acids, of $K_a = 10^{-10}$ and less, the hydrolysis of the salt formed becomes considerable and this will increase the pH above that calculated from the simple formula. The neutralisation curves of such extremely weak acids depend upon the concentrations employed and lie in the extreme alkaline part of the diagram. The opposite is true of extremely weak bases. In the case of a very weak acid the fact that alkaline solutions are produced when alkali is added shows that not all the acid could have combined to form a neutral salt. The amount unreacted upon can, however, be ascertained from the pH and the degree of ionisation of the alkali in such a dilution. The dissociation constant of the acid can then be calculated, being equal to

$$\frac{[\text{H}^{\cdot}][x-y]}{[\text{HR}] - [x-y]},$$

where [HR] is the original concentration of acid, x is the concentration of alkali added and y the concentration of alkali found from the pH to have remained uncombined.

The dissociation constants of extremely weak bases can be found in a similar manner. *The evaluation of these constants is of fundamental importance in connexion with the method of estimating weak acids or bases*, to be described later.

Hence, we see that the neutralisation curve of an acid, HR, with NaOH depends upon K_a, not only in regard to its position upon the pH scale, but also in regard to the shape which it will assume. For moderately strong acids, having affinity constants greater than about 10^{-4}, the hydrogen-ions and the anions liberated from the unneutralised acid acquire such relatively large concentrations depending upon the dilution of the solution that they invalidate the simple expression,

$$K_a = [\text{H}^{\cdot}] \times \frac{[\text{salt}]}{[\text{acid}]}$$

which we have found to hold for weak acids in which the unneutralised portions yield negligibly small hydrogen-ion concentrations. For these strong acids, we must include the concentrations of anions, $[R_u]$, dissociated from the unneutralised acid and of the undissociated acid which remains, thus :

$$K_a = [\text{H}^{\cdot}] \times \frac{[\text{salt}] + [R_u']}{[\text{acid}] - [R_u']} = \frac{[\text{H}^{\cdot}][\text{R}']}{[\text{HR}]}.$$

Towards the end of the neutralisation of a weak acid the salt formed from the alkali begins to hydrolyse, while in the case of an extremely weak acid considerable hydrolysis occurs throughout the whole course of the neutralisation, and therefore

$$K_a = [H^{\cdot}] \times \frac{[salt] - [OH']}{[acid] + [OH']} = \frac{[H^{\cdot}] \cdot [R']}{[HR]}.$$

Similar considerations are necessary with regard to the neutralisation of bases of differing strengths.

We shall now consider certain important pH values which are established at various stages of neutralisation of an acid. As

$$K_a = [H^{\cdot}] \times \frac{[R']}{[HR]},$$

therefore

$$p\mathrm{H} = pK_a + \log \frac{[R']}{[HR]},$$

so that, *for moderately strong acids mixed with their respective salts of strong bases,*

$$p\mathrm{H} = pK_a + \log \frac{[salt] + [R_u']}{[acid] - [R_u']},$$

for weak acids in presence of their respective salts of strong bases,

$$p\mathrm{H} = pK_a + \log \frac{[salt]}{[acid]},$$

for extremely weak acid solutions containing their respective salts of strong bases,

$$p\mathrm{H} = pK_a + \log \frac{[salt] - [OH']}{[acid] + [OH']}.$$

When $\qquad\qquad [R'] = [HR],$
we see that $\qquad\quad K_a = [H^{\cdot}],$
and $\qquad\qquad\quad pK_a = p\mathrm{H}.$

In connexion with the partly neutralised strong acids, this pH value is of little importance as it varies with concentration, but in the case of weak and extremely weak acids it marks the point at which the acids become half neutralised. For weak acids [salt] is then equal to [acid], and thus it follows that this pH is independent of concentration. In the case of very weak acids, [salt], *i.e.*, the concentration of neutral, or unhydrolysed, salt, does not become equal to [acid] when one half of an equivalent of sodium hydroxide has been added. Nevertheless, pK_a denotes the pH value when

one half of an equivalent of alkali has actually reacted, and as we shall see later this fixed pH is of fundamental importance in the titration of such extremely weak acids. Therefore, this particular pH fixes the positions of the actual neutralisation curves of all acids except those which are appreciably dissociated, and whose ionisations are not depressed sufficiently by the anions arising from their salts. Moreover, their actual neutralisation curves are fixed as

$$pH = pK_a + \log \frac{[\text{unhydrolysed salt}]}{[\text{undissociated acid}]}.$$

Table 18 gives the variations of pH from pK_a for different percentages of [salt] and [acid], and in effect represents the titration curve of a weak acid.

TABLE 18.

pH Values during Neutralisation of Weak Acid, HR, whose Constant is K_a.

Per cent. Neutralised (*i.e.*, per cent. Salt Formed).	pH.	Increment in pH per 5 per cent. Neutralisation.	Solutions.
0·01	$pK_a - 4·00$		Unbuffered
0·1	$pK_a - 3·00$		,,
1·0	$pK_a - 2·00$	$+ 2·72$	,,
2·5	$pK_a - 1·59$		,,
5	$pK_a - 1·28$		,,
10	$pK_a - 0·95$	$+ 0·33$	Buffered
15	$pK_a - 0·75$	$+ 0·20$	,,
20	$pK_a - 0·60$	$+ 0·15$	,,
25	$pK_a - 0·48$	$+ 0·12$	,,
30	$pK_a - 0·37$	$+ 0·11$	,,
35	$pK_a - 0·27$	$+ 0·10$	,,
40	$pK_a - 0·17$	$+ 0·10$	,,
45	$pK_a - 0·09$	$+ 0·08$	,,
50	$pK_a \mp 0·00$	$+ 0·09$	,,
55	$pK_a + 0·09$	$+ 0·09$	,,
60	$pK_a + 0·17$	$+ 0·08$	,,
65	$pK_a + 0·27$	$+ 0·10$	,,
70	$pK_a + 0·37$	$+ 0·10$	,,
75	$pK_a + 0·48$	$+ 0·11$	,,
80	$pK_a + 0·60$	$+ 0·12$	,,
85	$pK_a + 0·75$	$+ 0·15$	,,
90	$pK_a + 0·95$	$+ 0·20$	,,
95	$pK_a + 1·28$	$+ 0·33$	,,
97·5	$pK_a + 1·59$		Unbuffered
99·0	$pK_a + 2·00$	$+ 2·72$	,,
99·9	$pK_a + 3·00$		,,
99·99	$pK_a + 4·00$		,,

It will be observed from Table 18 that there should be well-defined ranges of pH values within which weak and extremely

weak acids are neutralised. This is the case, and as the mass law holds throughout these neutralisation reactions, the neutralisation pH range can be stated accurately if the constant, K_a, be known. Thus, if we consider the beginning of titration to occur when 0·01 per cent. of the acid has been reacted upon, the pH would be pK$_a$ — 4, and to end when 99·99 per cent. has been neutralised, the final pH would be pK$_a$ + 4, and the total pH range would be

$$(p\text{K}_a + 4) - (p\text{K}_a - 4) = 8\,p\text{H units.}$$

Such limits are extensive, and moreover, unnecessarily wide. Both at the beginning and at the end of a neutralisation very rapid changes in pH are produced with only very slight additions of alkali—there being 2 pH units change produced by an addition from 0·01 per cent. to 1 per cent. of alkali at the two extreme ends. If, however, we regard the neutralisation process to begin when 1 per cent. of alkali has been added and has formed the salt, and to finish at 99 per cent., we find that the

and the
$$\begin{aligned} &\textit{Initial } p\text{H} = p\text{K}_a - 2, \\ &\textit{Final } p\text{H} = p\text{K}_a + 2, \end{aligned}$$

and therefore, the *range of pH values required for neutralisation* to be

$$(p\text{K}_a + 2) - (p\text{K}_a - 2) = 4\,p\text{H units} = p\text{K}_a \mp 2.$$

This relationship is of practical importance and will be considered later.

Similar relationships hold for weak and very weak bases throughout their courses of neutralisation with a strong acid such as hydrochloric acid. Thus

$$\text{K}_b = \frac{[\text{B}^{\cdot}][\text{OH}']}{[\text{BOH}]}$$

holds for the dissociation of a base BOH as represented

$$\text{BOH} \rightleftharpoons \text{B}^{\cdot} + \text{OH}'.$$

Hence, we may write

$$\text{K}_b = [\text{OH}'] \times \frac{[\text{B}^{\cdot}]}{[\text{BOH}]} = [\text{OH}'] \times \frac{[\text{unhydrolysed salt}]}{[\text{undissociated base}]},$$

and therefore

$$p\text{OH} = p\text{K}_b + \log \frac{[\text{salt}]}{[\text{base}]}.$$

At the mid-point of neutralisation $\dfrac{[\text{salt}]}{[\text{base}]} = 1$, consequently

$$pOH = pK_b,$$

and as
$$K_w = [H^\cdot].[OH'],$$

i.e.,
$$pH + pOH = pK_w,$$

therefore, the pH corresponding to pK_b is given by

$$pH = pK_w - pK_b.$$

As the initial pOH (i.e., at 1 per cent. neutralisation) of the titration of a base is given by $pK_b - 2$, and the final pOH by $pK_b + 2$ (i.e., 99 per cent. neutralisation), we see that in terms of hydrogen-ion concentration the

$$Initial\ pH = pK_w - pK_b + 2,$$

the
$$Final\ pH = pK_w - pK_b - 2,$$

and the
$$Titration\ Range = pK_w - pK_b \pm 2.$$

Buffer Action.

Though this subject will receive further treatment in the next chapter, we shall accord it a preliminary treatment here. On referring to the third column of Table 18 it will be observed that the pH increment corresponding to each 5 per cent. of neutralisation of the acid, HR, is of the order of 0·1 pH unit over the range extending from about 20 per cent. to about 80 per cent. of neutralisation—in fact the variation in pH is approximately a linear function of the amount of alkali added. Thus we see that alkali when added to a solution containing a weak acid partly neutralised within these limits will not, unless it is added in excess, exert any great influence on the concentration of hydrogen-ions of the solution, i.e., it will cause only a very little change in the " reaction " or pH value of the solution. On the other hand, very small additions of alkali will produce considerable pH changes if the solution contains either free acid or almost completely neutralised acid. Similar remarks apply to the addition of strong acids to such solutions, and also to the variations in hydrogen-ion concentration which may be set up in solutions of weak bases neutralised to differing extents. Moreover, we know that if a little free NaOH or HCl be added to distilled water, pH ca. 7, there will result a very large and sudden increase or decrease in pH as the case may be.

As far back as 1900 Fernbach and Hubert (Comp. rend., 1900, 131, 293), in the course of some work on the diastatic activity of malt, observed that partly neutralised solutions of phosphoric acid (see Fig. 41) tended to resist changes in hydrogen-ion concentration, and they compared this resistance to that exerted by " un tampon."

Sørensen, later, used this term, which was translated into German as *Puffer*, and subsequently into English as " buffer." Hence this " buffer action " is pronounced in the case of solutions of weak acids or bases which have been neutralised to extents varying from 20 to 80 per cent. It attains to a maximum, as shown by Table 18, in an acid or base solution which has been half-neutralised. The figures given in column 3 constitute a measure of this action, for they indicate the change in pH produced by the additions of equal amounts of alkali. Actually, they are a measure of the slope of the neutralisation curve at the various points for they are the tangents of the angles made by the tangents drawn to the curve and the abscissa, *i.e.*, they are equal to $\dfrac{dp\mathrm{H}}{dx}$, dx being a small increment of alkali (or acid) added. It is sometimes more convenient to speak of the Buffer-Capacity of a solution, and for this purpose to know the amount of an acid or alkali of some definite concentration which must be added to produce a change in hydrogen-ion concentration represented by 1 pH unit. In a more restricted sense, this so-called " buffer-capacity " is given by $\dfrac{dx}{dp\mathrm{H}}$, and then it refers to the reciprocal of the tangent (*i.e.*, cotangent) of the angle of the slope of the curve at the point corresponding to the composition of the particular " buffer-solution." Unless the concentration of the buffering agents is large compared with that of the acid or alkali to be added, the buffer-capacity may undergo appreciable changes in value as the reagent is added. It is only, therefore, in the case of solutions of high buffer concentration, that such a function has any real meaning. It very often happens in biological operations that enzymes or bacteria require a definite small pH range for their optimum action or growth, and yet they cause substances to be developed, which if there were no buffering agents present in the solution would produce an unsuitable pH reaction. As will be shown later, controlled hydrogen-ion concentrations are of fundamental importance in analytical processes. Such control is often effected by the inclusion of buffering agents in the solutions ; in fact, many of the methods, which were developed quite empirically, depend solely upon the efficiency of the buffer action of the reagents.

Detection of Volumetric Titration End-Points.

It will be understood from the foregoing discussion that it is an easy matter to stipulate when the titration of a weak acid or base will be complete for all practical purposes (*viz.*, 99 per cent.), and therefore to choose an indicator which will turn colour at that

particular pH, or better, a little after that stage has been reached. The table of indicators affixed to Fig. 36 show the pH's at which they may each be used. Now, methyl orange is often used as an indicator in the titration of strong acids, but it will be seen from two curves at the base of the diagram that if the solution be as dilute as N/100 the methyl orange will begin to change colour on account of pH 2·9 being attained some time before neutralisation has become complete—and, indeed, it will hardly be complete when the colour has been completely changed. Centimolar solutions of strong acids represent the limit of concentration which can be used with methyl orange. Methyl red would appear to be more satisfactory, but, as may be seen from the neutralisation curve of carbonic acid, Fig. 37, its end-point will be affected by any carbon dioxide which may be present in the solution. The following tables, 19, 20, 21, 22, 23 and 24 give the dissociation

TABLE 19.

MONOBASIC ACIDS.

Name.	Formula.	K_a.	pK_a.
Hydrochloric acid	HCl	—	—
Nitric acid	HNO_3	—	—
Picric acid	$C_6H_2(NO_2)_3OH$	—	—
Trichloracetic acid	$CCl_3 \cdot COOH$	3	—
Dichloracetic acid	$CHCl_2 \cdot COOH$	5×10^{-2}	—
Monochloracetic acid	$CH_2Cl \cdot COOH$	$1·6 \times 10^{-3}$	—
Salicylic acid	$C_6H_4(OH)COOH$	1×10^{-3}	3
Nitrous acid	HNO_2	5×10^{-4}	3·3
Formic acid	$H \cdot COOH$	2×10^{-4}	3·7
Glycollic acid	$CH_2OH \cdot COOH$	$1·5 \times 10^{-4}$	3·8
Lactic acid	$CH_3 \cdot CHOH \cdot COOH$	$1·4 \times 10^{-4}$	3·8
Benzoic acid	$C_6H_5 \cdot COOH$	7×10^{-5}	4·2
Phenylacetic acid	$C_6H_5CH_2COOH$	$5·4 \times 10^{-5}$	4·3
Acetic acid	$CH_3 \cdot COOH$	$1·8 \times 10^{-5}$	4·7
Hydrazoic acid	HN_3	$1·5 \times 10^{-5}$	4·8
Propionic acid	$C_2H_5 \cdot COOH$	$1·4 \times 10^{-5}$	4·8
Uric acid	$C_5H_4N_4O_3$	$1·5 \times 10^{-6}$	5·8
o-Nitro-phenol	$C_6H_4(NO_2)OH$	$5·6 \times 10^{-8}$	7·3
p-Nitro-phenol	$C_6H_4(NO_2)OH$	$5·6 \times 10^{-8}$	7·3
Hypochlorous acid	HClO	4×10^{-8}	7·4
m-Nitro-phenol	$C_6H_4(NO_2)OH$	$3·9 \times 10^{-9}$	8·4
Hydrocyanic acid	HCN	1×10^{-9}	9
Boric acid	$HBO_2 \cdot H_2O$	6×10^{-10}	9·2
p-Chlorophenol	$C_6H_4 \cdot Cl \cdot OH$	6×10^{-10}	9·2
Phenol	$C_6H_5 \cdot OH$	1×10^{-10}	10
Hydrogen peroxide	H_2O_2	1×10^{-12}	12
Dextrose	$C_6H_7O(OH)_5$	$5·8 \times 10^{-13}$	12·2
Cane sugar, sucrose	$C_{12}H_{22}O_{11}$	1×10^{-13}	13
Mannitol	$C_6H_8(OH)_6$	3×10^{-11}	13·5
Glycerol	$C_3H_5(OH)_3$	7×10^{-15}	14·2
Glycol	$C_2H_4(OH)_2$	6×10^{-15}	14·2

TABLE 20.

DIBASIC ACIDS.

Name.		K_{a_1}.	pK_{a_1}.	K_{a_2}.	pK_{a_2}.	$\dfrac{K_{a_1}}{K_{a_2}}$
Oxalic acid	$(COOH)_2$	1×10^{-2}	—	$1 \cdot 3 \times 10^{-4}$	$3 \cdot 9$	$ca.\ 1{,}000$
Chromic acid	H_2CrO_4	—	—	$4 \cdot 4 \times 10^{-7}$	$6 \cdot 4$	$ca.\ 10^6$
Sulphurous acid	H_2SO_3	$1 \cdot 7 \times 10^{-2}$	—	5×10^{-6}	$5 \cdot 3$	$3{,}400$
Dibromsuccinic acid	$C_2H_2Br_2(COOH)_2$	$3 \cdot 4 \times 10^{-2}$	—	$1 \cdot 6 \times 10^{-3}$	—	21
Monobrom-succinic acid	$C_2H_3Br(COOH)_2$	$2 \cdot 8 \times 10^{-3}$	$2 \cdot 6$	$3 \cdot 9 \times 10^{-5}$	$4 \cdot 4$	72
Succinic acid	$(CH_2)_2(COOH)_2$	$9 \cdot 2 \times 10^{-5}$	$4 \cdot 0$	$5 \cdot 3 \times 10^{-6}$	$5 \cdot 3$	17
Tartaric acid	$C_2H_2(OH)_2 \cdot (COOH)_2$	$1 \cdot 3 \times 10^{-3}$	$2 \cdot 9$	$9 \cdot 7 \times 10^{-5}$	$4 \cdot 0$	13
Maleic acid	$C_2H_2 \cdot (COOH)_2$	$1 \cdot 3 \times 10^{-2}$	$2 \cdot 9$	$3 \cdot 0 \times 10^{-7}$	$6 \cdot 5$	$4 \cdot 3 \times 10^4$
Fumaric acid	$C_2H_2 \cdot (COOH)_2$	1×10^{-3}	$3 \cdot 0$	$2 \cdot 5 \times 10^{-5}$	$4 \cdot 6$	40
o-Phthalic acid	$C_6H_4 \cdot (COOH)_2$	$1 \cdot 2 \times 10^{-3}$	$2 \cdot 9$	$8 \cdot 0 \times 10^{-6}$	$5 \cdot 1$	150
m-Phthalic acid	$C_6H_4 \cdot (COOH)_2$	$2 \cdot 9 \times 10^{-4}$	$3 \cdot 5$	$2 \cdot 4 \times 10^{-5}$	$4 \cdot 6$	12
Carbonic acid	H_2CO_3	3×10^{-7}	$6 \cdot 5$	6×10^{-11}	$10 \cdot 2$	$5{,}000$
Hydrosulphuric acid	H_2S	9×10^{-8}	$7 \cdot 0$	$1 \cdot 2 \times 10^{-15}$	$14 \cdot 9$	$7 \cdot 5 \times 10^7$
Malonic acid	$CH_2 \cdot (COOH)_2$	$2 \cdot 0 \times 10^{-3}$	$2 \cdot 7$	$4 \cdot 4 \times 10^{-6}$	$5 \cdot 4$	460
Glutaric acid	$(CH_2)_3 \cdot (COOH)_2$	$4 \cdot 7 \times 10^{-5}$	$4 \cdot 3$	$2 \cdot 9 \times 10^{-6}$	$5 \cdot 5$	16
Suberic acid	$(CH_2)_6 \cdot (COOH)_2$	$3 \cdot 0 \times 10^{-5}$	$4 \cdot 5$	$1 \cdot 9 \times 10^{-6}$	$5 \cdot 7$	16
Azelaic acid	$(CH_2)_7 \cdot (COOH)_2$	$2 \cdot 5 \times 10^{-5}$	$4 \cdot 6$	$2 \cdot 4 \times 10^{-6}$	$5 \cdot 6$	10
Sebacic acid	$(CH_2)_8 \cdot (COOH)_2$	$2 \cdot 4 \times 10^{-5}$	$4 \cdot 6$	$2 \cdot 5 \times 10^{-6}$	$5 \cdot 6$	10

TABLE 21.

TRIBASIC ACIDS.

Name.	K_1.	pK_1.	K_2.	pK_2.	K_2.	pK_3.
Phosphoric acid	$9 \cdot 4 \times 10^{-3}$	—	$1 \cdot 4 \times 10^{-7}$	$6 \cdot 9$	$2 \cdot 7 \times 10^{-12}$	$11 \cdot 6$
Citric acid	$1 \cdot 0 \times 10^{-3}$	$3 \cdot 0$	$2 \cdot 5 \times 10^{-5}$	$4 \cdot 6$	$1 \cdot 5 \times 10^{-6}$	$5 \cdot 8$

TABLE 22.

MONO-ACIDIC BASES.

Name.	K_b.	pK_b.
Ammonia	$1 \cdot 8 \times 10^{-5}$	4·7
Hydrazine	$2 \quad \times 10^{-6}$	5·7
Phenylhydrazine	$1 \cdot 6 \times 10^{-9} (40°)$	8·8
Methylamine	$5 \quad \times 10^{-4}$	3·3
Dimethylamine	$5 \cdot 5 \times 10^{-4}$	3·3
Trimethylamine	$7 \quad \times 10^{-5}$	4·2
Ethylamine	$5 \cdot 6 \times 10^{-4}$	3·3
Diethylamine	$1 \cdot 3 \times 10^{-3}$	2·9
Triethylamine	$6 \cdot 4 \times 10^{-4}$	3·2
Aniline	$3 \cdot 5 \times 10^{-10}$	9·5
o-Nitro-aniline	$1 \quad \times 10^{-14}$	14
m-Nitro-aniline	$3 \cdot 6 \times 10^{-12}$	11·4
p-Nitro-aniline	$1 \quad \times 10^{-12}$	12
m-Bromoaniline	$3 \cdot 8 \times 10^{-11}$	10·4
p-Bromoaniline	$1 \quad \times 10^{-10}$	10
m-Chloroaniline	$3 \cdot 4 \times 10^{-11}$	10·5
p-Chloroaniline	$1 \cdot 5 \times 10^{-10}$	9·8
Acetamide	$3 \quad \times 10^{-15}$	14·5
Pyridine	$1 \cdot 2 \times 10^{-9}$	8·9
Piperidine	$1 \cdot 6 \times 10^{-3}$	2·8
Quinoline	$3 \cdot 2 \times 10^{-10}$	9·5
Isoquinoline	$1 \cdot 1 \times 10^{-9}$	9
Conine	$8 \quad \times 10^{-4}$	3·1
Atropine	$4 \cdot 5 \times 10^{-5}$	4·4
Cocaine	$2 \cdot 6 \times 10^{-6}$	5·6
Narcotine	$1 \cdot 5 \times 10^{-8}$	7·8
Codeine	$9 \quad \times 10^{-7}$	6·1
Aconitine	$1 \cdot 3 \times 10^{-6}$	5·9

TABLE 23.

DIACIDIC BASES.

Name.	K_{b_1}.	pK_{b_1}.	K_{b_2}.	pK_{b_2}.	$\dfrac{K_{b_1}}{K_{b_2}}$.
Piperazine	$9 \quad \times 10^{-5}$	4·1	$5 \cdot 7 \times 10^{-9}$	8·3	$1 \cdot 6 \times 10^{4}$
Novocain	$7 \cdot 1 \times 10^{-6}$	5·2	$1 \cdot 8 \times 10^{-12}$	11·8	$4 \quad \times 10^{6}$
Nicotine	$7 \quad \times 10^{-7}$	6·2	$1 \cdot 4 \times 10^{-11}$	10·9	$5 \quad \times 10^{4}$
Quinine	$1 \cdot 1 \times 10^{-6}$	6	$2 \quad \times 10^{-10}$	9·7	$5 \cdot 5 \times 10^{3}$
Cinchonidine	$1 \cdot 6 \times 10^{-6}$	5·8	$9 \cdot 3 \times 10^{-11}$	10	$1 \cdot 7 \times 10^{4}$
Cinchonine	$1 \cdot 4 \times 10^{-6}$	5·9	$1 \cdot 2 \times 10^{-10}$	9·9	$1 \cdot 2 \times 10^{4}$
Strychnine	$1 \quad \times 10^{-6}$	6	$2 \cdot 2 \times 10^{-12}$	11·7	$4 \cdot 5 \times 10^{5}$
Brucine	$9 \cdot 2 \times 10^{-7}$	6	$2 \quad \times 10^{-12}$	11·7	$4 \cdot 6 \times 10^{5}$
Pilocarpine	$7 \quad \times 10^{-8}$	7·2	$2 \cdot 7 \times 10^{-13}$	12·6	$2 \cdot 6 \times 10^{5}$

TABLE 24.

AMPHOLYTES.

	K_a	pK_a	K_b	pK_b
Morphine*	1.4×10^{-10}	9.85	7.5×10^{-7}	6.13
Apomorphine*	1.2×10^{-9}	8.92	1×10^{-7}	7
Narcein	5×10^{-10}	9.3	2×10^{-11}	10.7
Ecgonine	8×10^{-12}	11.1	6×10^{-12}	11.2
α-Alanine	1.9×10^{-10}	9.7	5.1×10^{-12}	11.3
Glycine	1.8×10^{-10}	9.7	2.7×10^{-12}	11.6
Leucine	1.8×10^{-10}	9.7	2.3×10^{-12}	11.6
Phenyl-alanine	2.5×10^{-9}	8.6	1.3×10^{-12}	11.9
Valine	2×10^{-10}	9.7	2×10^{-12}	11.7
m-Aminobenzoic acid	1.6×10^{-5}	4.8	1.2×10^{-12}	11.9

AMINO-DICARBOXYLIC ACIDS.

	K_{a_1}	pK_{a_1}	K_{a_2}	pK_{a_2}	K_b	pK_b
Glutamic acid	6.2×10^{-5}	4.2	1.6×10^{-10}	9.8	1.3×10^{-12}	11.9
Aspartic acid	1.5×10^{-4}	3.8	1.4×10^{-10}	9.9	1.2×10^{-12}	11.9
Tyrosine*	4×10^{-10}	9.4	4×10^{-11}	10.4	2.6×10^{-12}	11.6

* One K_a refers to the dissociation of a phenolic group.

DIAMINO-CARBOXYLIC ACIDS.

	K_a	pK_a	K_{b_1}	pK_{b_1}	K_{b_2}	pK_{b_2}
Histidine	2.2×10^{-9}	8.7	5.7×10^{-9}	8.2	5×10^{-13}	12.3
Arginine	$>1.1 \times 10^{-14}$	14	$<1 \times 10^{-7}$	7	2.2×10^{-12}	11.7
Lysine	$1-2 \times 10^{-12}$	12	$<1 \times 10^{-7}$	7	1.1×10^{-12}	12

constants of various typical acids, bases and ampholytes, and also the value of pK, which, as shown above, is the pH prevailing when a weak acid, and the pOH when a weak base, has been half-neutralised, and in the case of polybasic acids or bases, at the mid-point of each stage of neutralisation. In the case of extremely weak acids and bases the stage of half-neutralisation does not occur when the alkali or acid added is the quantity theoretically required on account of the hydrolysis of the salt formed, but occurs when more reagent, sufficient to counteract that hydrolysis, has been added.

The actual end-point pH's in the neutralisation of weak acids with a strong base are given by

$$pH = pK_a + 2,$$

and the titration end-points of weak bases with strong acids by

$$pH = pK_w - pK_b - 2.$$

They may, however, be judged with sufficient accuracy from Fig. 36. Thus, the neutralisation curve of acetic acid, Table 8, $pK_a = 4.7$, will be just below that corresponding to $K_a = 10^{-5}$, and, consequently, for its volumetric estimation an indicator will be required which turns colour above pH 6, such as Cresol Red or Phenolphthalein.

It might be surpising to some to find such substances as hydrogen peroxide, sugars and glycerol included in the table of monobasic acids. Though they possess measurable acidic natures, the dissociation constants are so low that on neutralisation with alkali they give buffered pH curves which merge into that given when an excess of alkali has been added without producing an inflexion. These curves would lie at the top of Fig. 36, and therefore prevent the estimation of acids by the ordinary method of volumetric analysis, though approximate estimations of the acidic substances can be made by colorimetric determinations of pH with, say Tropæolin O on adding varying amounts of alkali.

Di- and Tribasic Acids.

Tables 20 and 21 refer to dibasic and tribasic acids, and, needless to say that, in order to ascertain what indicator should be used for the complete titration of the acid, it is only necessary to consider the magnitude of the final dissociation constant. Thus, pK_{a_2} for chromic acid is 6.4, and the neutralisation curve for the second half will lie almost midway between the 10^{-6} and 10^{-7} curves, the pH at complete neutralisation being about 9, and, consequently, if phenolphthalein be used it will begin to redden slightly before the true end-point is reached. A more satisfactory indicator would be thymolphthalein.

It is often possible to titrate certain polybasic acids and polyacidic bases to an intermediate end-point corresponding to the formation of, in the former case, an acid salt, and in the latter, a basic salt. This possibility will be studied in a subsequent paragraph. It will be observed from Table 21 that the last dissociation constant of phosphoric acid is so excessively small that its neutralisation is not complete until pH 13.6 is reached—

a value which is outside the range of indicators and especially as the final branch of the neutralisation curve merges into the alkali curve, giving no inflexion.

Bases and Alkaloids.

Tables 22 and 23 give the affinity constants of mono- and di-acidic bases respectively. It will be noticed that the alkaloids appear in these tables ; the results were taken from an important paper by Kolthoff (*Biochemische Z.*, 1925, **162**, 289), which gives the constants for many other alkaloids, including their solu- bilities and solu- bility products.

One of the most accurate methods for the estimation of alkaloids is by titration, though it is here that the problem of indi- cators becomes of fundamental im- portance. Thus MacGill (*J. Amer. Chem. Soc.*, 1922, **44**, 2156) has shown that the in- dicators used in the titration of morphine, atro- pine and quinine
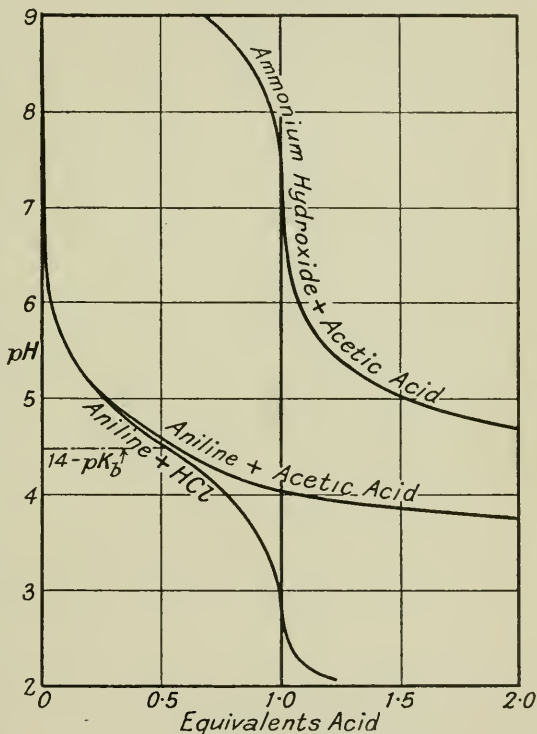
FIG. 37.—Titration of Weak Bases.

give results which are not nearly as accurate as could be obtained with more appropriate indicators. In the case of morphine the average error using methyl red was 1·4 per cent., whereas bromophenol blue gave an average error of 0·5 per cent., and in some cases it was as low as 0·1 per cent. Kolthoff recom- mends that the indicator to be used with all mono-acidic bases having K_b equal to or greater than 5×10^{-7} should be methyl red. This will be obvious from Fig. 36, for all curves lying above that of K_b $10^{-6\cdot3}$ show that neutralisation becomes complete

above or at pH 5, the change-point of methyl-red. For weaker bases indicators changing at a lower pH, such as methyl orange or bromophenol blue will be necessary. Aniline and the substituted aniline derivatives have very small constants, so much so that it appears from Fig. 36 that the pH inflexion on complete neutralisation with acid will be so very small as to render the locating of the end-point with any accuracy by means of indicators a matter of extreme difficulty. Another matter which militates against the use of indicators with aniline is the tendency which it has to redden and thus to obscure the colour change. As stated by Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35,** 847) the location of the end-point can best be made electrometrically (see Fig. 37). The remarks concerning the variation in pH during the neutralisation of dibasic acids also hold for diacidic bases, but as shown in the last column of Table 23, K_{b_2} is often so very small compared with K_{b_1} that a sharp pH inflexion occurs with the neutralisation of the first stage, which, by reason of the magnitude of K_{b1} (pK$_{b1}$ being usually about 6) permits of its titration to methyl red, before the second and considerably weaker stage enters into the reaction. Rasmussen and Schou (*Pharm. Zentralhalle*, 1924, **65,** 729) advocate methyl red with strychnine, brucine, morphine, codeine, nicotine, and atropine ; methyl orange buffered to pH 4·2 for narcotine and p-nitrophenol buffered to pH 6·2 for quinine. These end-points are in accord with Fig. 36 and the data given in the tables.

The basic dissociation constants of the alkaloids also supply information which may be of importance in connexion with their separation. Thus, for example, consider a mixture of the salts of two alkaloids having dissociation constants widely different and which are both soluble in an organic solvent. On treatment with an alkali, the salt whose alkaloid has the correct dissociation constant will first be reacted upon and then dissolved in the organic solvent before the second salt becomes decomposed. The difficulty arises, however, of knowing when to stop adding alkali in order to prevent the liberation of the second base. From a knowledge of the basic constants it may be possible to employ a solution buffered within a small pH range instead of the free alkali and thereby to prevent the second base from being extracted (see Evers, *Yearbook of Pharmacy*, 1922). Again, it is possible that use will be made of the solubility products of the alkaloids, coupled with their dissociation constants, to separate them from their salt solutions by means of fractional precipitation with alkali, or better with suitably buffered solutions. The work of Mauz (*Physik-Chem. Untersuchungen über Alkaloide*, Dissertation,

Stuttgart, 1904, cited by Kolthoff (*loc. cit.*)) has indicated the possibilities of such methods.

Ampholytes.

Table 24 supplies data relating to bodies which are amphoteric, *i.e.*, which are capable of behaving as either a base or an acid, sometimes with several stages of reactivity as a base or as an acid. Thus towards alkalis they behave as acids and as bases when treated with acids. Often both the acidic and basic constants are very small, and excepting a few instances such as morphine, apomorphine, glutamic and aspartic acids, are too small to permit of titration by means of indicators.

Sørensen's Formol Titration.

Sørensen (*Biochem. Z.*, 1907, **7**, 45) found that if an excess of neutralised formaldehyde be added to a solution of an ampholyte it then became possible to titrate the carboxyl group to phenolphthalein. Consider the simplest ampholyte, *viz.*, glycine. It will be concluded from the value of K_a, 1.8×10^{-10}, that only a slight pH inflexion will be produced when an excess of alkali is added, which will take place in relatively strongly alkaline solution at about pH 11, and thus be outside the range of ordinary indicators. The reaction with formaldehyde probably is the formation of methylene-imino group, $-N=CH_2$, in place of

TABLE 25.

APPROXIMATE DISSOCIATION CONSTANTS OF METHYLENE-IMINO DERIVATIVES OF AMINO-ACIDS.

Name.	Free Amino-Acid.		Methylene Derivative.		K Methylene-Acid. K Amino-Acid.
	K_a	pK$_a$	$K_{a'}$	pK$_{a'}$	
Glycine	2×10^{-10}	9·7	4×10^{-6}	5·4	10^4
Alanine	2×10^{-10}	9·7	5×10^{-7}	6·3	10^3
Phenyl-alanine	2.5×10^{-9}	8·6	1.3×10^{-6}	5·9	10^3
Tyrosine—					
Ka_1	4×10^{-10}	9·4	6.3×10^{-7}	6·2	10^3
Ka_2	4×10^{-11}	10·4	*ca.* 10^{-9}	*ca.* 9	—
Aspartic acid—					
Ka_1	1.5×10^{-4}	3·8	$> 10^{-3}$	<3	—
Ka_2	1.3×10^{-10}	9·9	1.3×10^{-7}	6·9	10^3
Glutamic acid—					
Ka_1	4×10^{-5}	4·4	$>3 \times 10^{-4}$	<3.5	—
Ka_2	1.6×10^{-10}	9·8	1.6×10^{-7}	6·8	10^3

the amino group. Harris (*Proc. Roy. Soc.*, 1925, **97**, B, 357) has found that the dissociation constants of these methylene-imino derivatives, given in Table 25 are usually of the order of 100c times the acidic constant of the parent acid. The effect, as will be seen from pK_a', is to bring the titration curve down to somewhere in the region of that of $K_a = 10^{-6}$, Fig. 36, and therefore to render the acid titratable to phenolphthalein.

Titration of Boric Acid.

Boric acid behaves as an extremely weak monobasic acid, HBO_2,H_2O, $K = 6 \times 10^{-10}$, and therefore gives an indefinite end-point in the region of pH 11, and as may be seen from the titration curve in Fig. 37 will cause phenolphthalein to turn colour when it is between 10 and 20 per cent. neutralised. It has long been known that if either glycerol or mannitol be added to the solution undergoing titration the pink colour disappears until the alkali has been added in an equivalent quantity. Hildebrand (*loc. cit.*) followed the change in pH when varying amounts of mannitol were added to a boric acid solution. The curves A, B, C, D, E, represent his observations. Curve E corresponds roughly to $K = 10^{-5}$, and thus the effect of the excess of mannitol was to magnify the K by about 10,000, and therefore boric acid can then be titrated to phenolphthalein. The explanation probably lies in the formation of a complex mannitol-boric acid, though Manganini (*Z. physikal. Chem.*, 1890, **6**, 58) found that although conductivity measurements gave evidence of some such combination in concentrated solutions, as soon as the boric acid solutions became dilute the complex acid must have become hydrolysed for the conducitivity measurements again became normal. Fox and Gauge (*J. Chem. Soc.*, 1911, **99**, 1075) prepared a crystalline body, $C_6H_{15}O_8B$, but from *alcoholic solutions*.

The carbonic acid neutralisation curve given on Fig. 38 shows the effect which any dissolved carbon dioxide will have on the accuracy of the boric acid estimation.

Titration of Solutions of either Mixed Acids or Mixed Bases.

Hitherto, we have confined our attention to the titration of single acids and bases, though if the solution contains two acids or two bases whose dissociation constants are sufficiently different the stronger acid or base will be neutralised before the reaction with the weaker component can begin. Hence the final pH of the effective titration range of the first acid, which is $pK_{a_1} + 2$

must be less than the initial pH of the titration range of the second acid, *viz.*, $p\mathrm{K}_{a_2} - 2$,

i.e.,
$$p\mathrm{K}_{a_2} - 2 > p\mathrm{K}_{a_1} + 2,$$
$$p\mathrm{K}_{a_2} - p\mathrm{K}_{a_1} > 4,$$

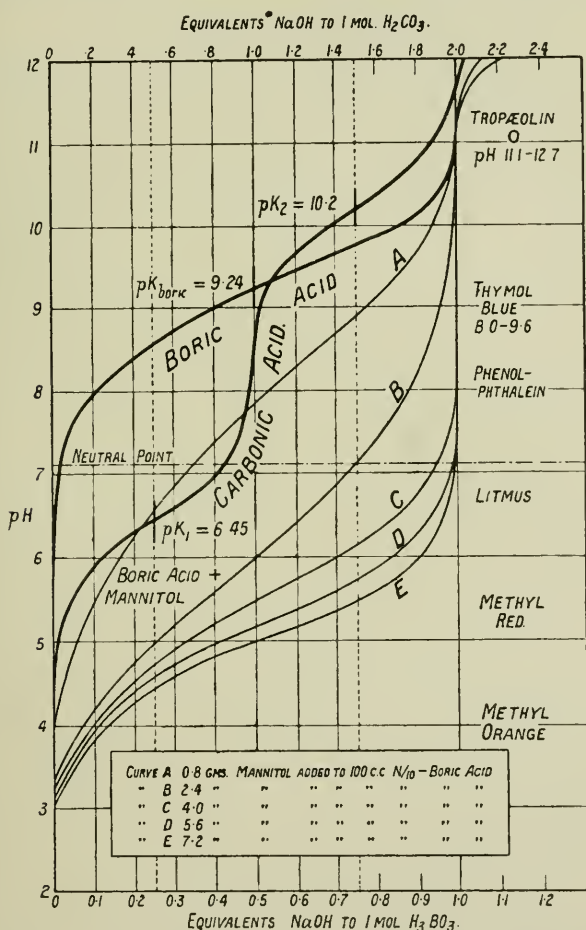and therefore K_{a_1}, the dissociation constant of the first acid must

FIG. 38.—Neutralisation Curves of Carbonic and Boric Acids.

be greater than 10,000 times K_{a_2}, the dissociation constant of the second acid.   Similar remarks apply to mixtures of bases.

When the constants are closer together, the end-points will

not be sharp through some of the weaker acid having begun to be neutralised before the stronger acid had been completely neutralised. When the first constant is not more than, say, 10 to 100 times the second, the titration curve may fail to show even a slight inflexion corresponding to the addition of reagent equivalent to the first component.

Electrometric Titration of Acids and Bases.

We shall now consider various typical electrometric pH neutralisation curves. In Fig. 39 curves of solutions of three weak monobasic acids
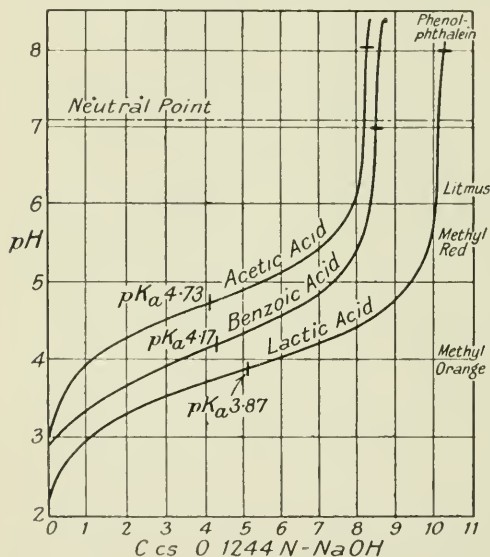
FIG. 39.—Quinhydrone Electrode Titration Curves of Monobasic Acids : 10 c.c. 1277 N-Lactic Acid ; 50 c.c. 0·02114 N-Benzoic Acid ; 10 c.c. 0·1025 N-Acetic Acid.

weak monobasic acids having different concentrations are given. These curves were drawn from data obtained with the quinhydrone electrode by Auerbach and Smolczyk (*Z. physikal. Chem.*, 1924, **110**, 83). The slightly different forms assumed by the first halves of the curves illustrate the effect of the acid concentration. The end-points were located by finding the points of inflexion of the upward curves. These can often be judged from the graph, but may be obtained with greater precision by calculating the tangent of the angle of slope of the curve until the point is found at which the tangent becomes of maximum value. This is the same as calculating $\frac{\delta E}{\delta x}$, where δE is the increase in voltage produced by adding a small increment, δx, of alkali, say 0·1 c.c. (*cf.* Hostetter and Roberts, *J. Amer. Chem. Soc.*, 1919, **41**, 1337). The neutralisation of the weak bases, ammonia and aniline, is represented in Fig. 37. As might have been predicted, it is possible to titrate ammonium hydroxide with acetic acid to an equivalence-point

which occurs sharply at approximately pH 7·5, in contrast with, for instance, the titration of hydrochloric acid in which case the actual end-point might be extended over a fairly wide pH range without introducing any great error.   For such a titration an electrometric method must be employed.   It might be possible, however, to perform such a titration by titrating to a definite colour of an indicator corresponding to some predetermined pH value, indicated by comparison with the colour obtained by adding a suitable quantity of indicator to a buffer solution adjusted to that pH.   Of the other curves, one shows that the magnitude of the decrease in pH which accompanies the formation of aniline hydrochloride is great
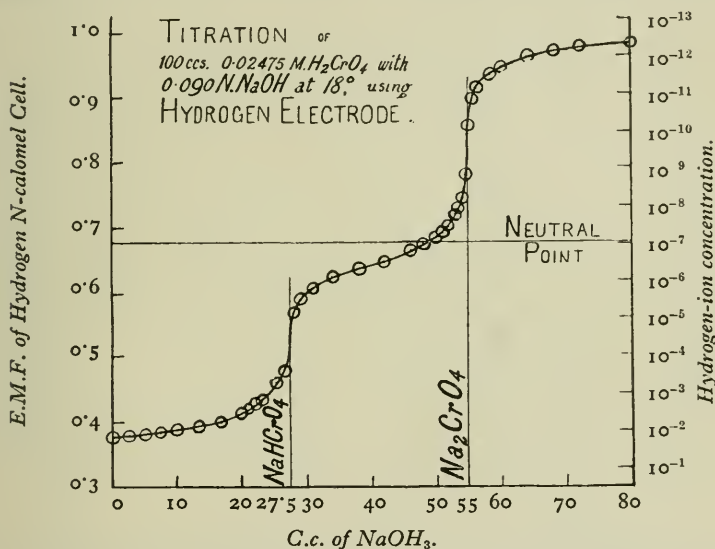
FIG. 40.—Hydrogen Electrode Titration of Chromic Acid (Britton, *J. Chem. Soc.*, 1924, **125**, 1572).

enough to permit of the electrometric titration of aniline, whilst the other curve illustrates that, owing to the large amount of hydrolysis of aniline acetate, much acetic acid fails to combine and so makes such a titration impossible.   This might have been foreseen from a consideration of the basic and acidic constants.

Electrometric titration curves of polybasic acids are given in Figs. 40 and 41.   Perhaps the simplest curve is that of chromic acid (Fig. 40).   On account of the failure to measure the extremely slight ionisation of the hydrochromate ion, $HCrO_4'$, it being much too small to have any influence upon the physical properties of free chromic acid solutions, *e.g.*, the conductivity in different

dilutions and the depression of the freezing-point, the dubious idea of the existence of dichromic acid was introduced by Ostwald (see Britton, *J. Chem. Soc.*, 1924, **125**, 1572). The curve shows that the first stage of chromic acid neutralisation is solely that of a strong monobasic acid, *viz.*, $H_2CrO_4 \rightleftharpoons H^{\cdot} + HCrO_4'$, whose dissociation constant is approximately one million times the second. The second branch corresponds entirely to that of the neutralisation of a weak monobasic acid. The two dissociation constants may therefore be calculated in the simple manner adopted for monobasic acids. The inflexion of the curve pro-
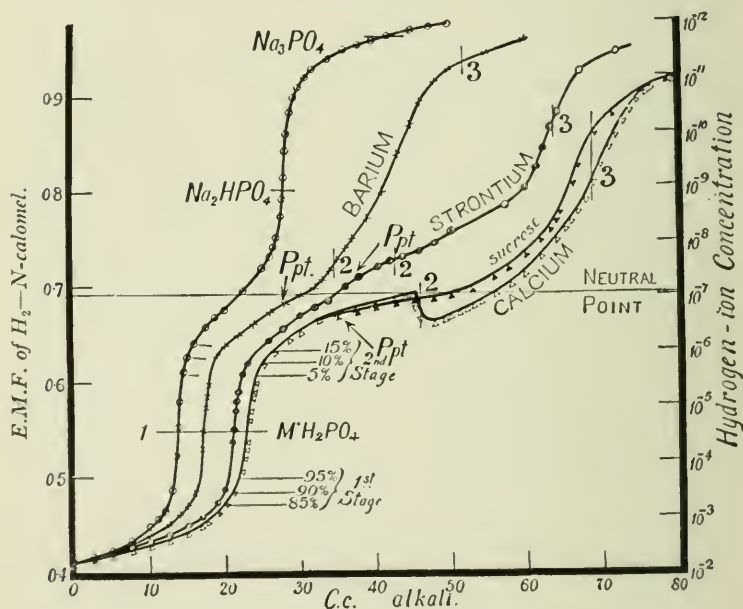
FIG. 41.—Hydrogen Electrode Titration Curves of Phosphoric Acid
(Britton, *J. Chem. Soc.*, 1927, 614).

duced at the end of the first half of the neutralisation shows that it is possible to titrate chromic acid to about pH 4·5 with methyl orange. A similar curve is given of phosphoric acid, Fig. 41. Each of the three stages of neutralisation are quite distinct from one another. Thus the first corresponds to the neutralisation of a strong acid, $H_3PO_4 \rightleftharpoons H^{\cdot} + H_2PO_4'$, the second to that of a weak acid, $H_2PO_4' \rightleftharpoons H^{\cdot} + HPO_4''$, and the last, whose curve is indistinguishable, on account of the excessive weakness of the acid and the resulting considerable hydrolysis, from the

TABLE 26.

TITRATION OF 100 C.C. OF 0·01277 M.-H_3PO_4 WITH 0·0919 N-NaOH AT 20°, WITH HYDROGEN ELECTRODE N-CALOMEL ELFCTRODE COMBINATION ($NaH_2PO_4 = 13·9$ C.C.; $Na_2HPO_4 = 27·8$ C.C.).

NaOH (c.c.).	E.M.F.	pH.	$[H_2PO_4'] \times 10^3$.	$[H_3PO_4] \times 10^3$.	$K_1 \times 10^3$.
0·0	0·408	2·14	7·24	5·53	9·55
2·55	0·416	2·28	7·54	4·92	8·13
5·0	0·423	2·40	8·36	3·80	8·71
7·5	0·433	2·57	9·10	2·78	8·91
10·0	0·447	2·81	9·90	1·71	9·12
11·0	0·455	2·94	10·26	1·24	9·55
12·0	0·464	3·10	10·64	0·76	11·22
13·0	0·486	3·48	10·90	0·36	10·00
13·5	0·521	4·10	11·00	0·26	3·31
				Mean	9·4

NaOH (c.c.).	E.M.F.	pH.	C.c. NaH_2PO_4.	C.c. Na_2HPO_4.	$K_2 \times 10^7$.
14·5	0·610	5·60	13·3	0·6	1·12
15·0	0·625	5·86	12·8	1·1	1·18
16·0	0·640	6·11	11·8	2·1	1·38
17·5	0·657	6·40	10·3	3·6	1·38
20·0	0·675	6·71	7·8	6·1	1·51
22·5	0·695	7·06	5·3	8·6	1·41
25·0	0·719	7·47	2·8	11·1	1·35
26·0	0·731	7·67	1·8	12·1	1·44
27·0	0·751	8·01	0·8	13·1	1·35
27·5	0·773	8·39	0·3	13·6	1·82
				Mean	1·4

NaOH (c.c.).	E.M.F.	pH.	$[PO_4'''] \times 10^3$.	$[HPO_4''] \times 10^3$.	$K_3 \times 10^{12}$.
29·0	0·883	10·28	0·66	9·24	3·72
30·0	0·909	10·72	1·02	8·80	2·24
31·0	0·921	10·92	1·42	8·33	2·04
32·0	0·928	11·05	1·80	7·87	2·04
34·0	0·940	11·26	2·43	7·10	1·91
36·0	0·949	11·40	3·03	6·36	1·91
38·0	0·954	11·49	3·70	5·55	2·19
40·0	0·959	11·57	4·29	4·83	2·40
42·5	0·964	11·66	4·91	4·05	2·63
45·0	0·968	11·72	5·65	3·16	3·39
47·5	0·973	11·81	5·81	2·85	3·16
50·0	0·975	11·85	6·52	1·99	4·57
				Mean	2·7

curve representing an excess of sodium hydroxide, to the neutralisation of an extremely weak acid, $HPO_4'' \rightleftharpoons H^{\boldsymbol\cdot} + PO_4'''$. The other curves show that when phosphoric acid is treated with either calcium, strontium or barium hydroxides, the first stage of the reaction is the formation of the soluble salt, $e.g.$, $Ca(H_2PO_4)_2$, but thereafter insoluble phosphates are formed. These will be referred to in Chapters XVIII, XXIV, XXVII and XXX. The titration curve of phosphoric acid may, therefore, be regarded as being composed of the curves of three separate mono-basic acids of widely different strengths. The complete data of the phosphoric acid-sodium hydroxide curve are given in Table 26. They are of interest in that they show how the different methods of calculation of the dissociation constants of monobasic acids described on page 129 have been applied.

The polybasic acids, which we have so far considered, have had widely differing dissociation constants governing their several stages of ionisation such that their titration curves were divided into well-defined sections similar to the neutralisation curves of weak monobasic acids. These curves are by no means typical of the neutralisation of polybasic acids, for as we shall see, the dissociation constants of successive stages of ionisation are often not so widely different that the neutralisation of the hydrogen-ions arising from the first step is completed before those from the second stage begin to enter into reaction. Fig. 42 gives the titration curves of four typical dibasic acids, and was taken from the author's paper, *J. Chem. Soc.*, 1925, **127**, 1896. Both oxalic and malonic acids gave inflexions when one equivalent of alkali had been added, but it will be observed that they are drawn out over a period corresponding to the addition of a fair amount of alkali. No inflexions were produced in the tartaric or succinic acid curves.

Before proceeding to discuss the construction of these curves, we shall consider the methods by which the dissociation constants of dibasic acids can be found. We shall ignore for the moment the fact that the second hydrogen-ion often comes into play long before half the stoichiometrical amount of alkali has been added, and calculate the constants in the manner adopted for phosphoric acid (Table 26).

The complete data of the neutralisation of tartaric acid are given in Table 27. The figures in the fifth column show the extent of the dissociation of the unneutralised acid as calculated from the observed E.M.F's of the hydrogen electrode compared with that of the normal calomel electrode. They show that as the titration proceeded the degree of ionisation diminished at first, and later appeared to increase. Though the value of K_1 remained

at 1.3×10^{-3} for the first three readings, it also appeared to increase for the subsequent additions of alkali. The assumption that the alkali, after 25 c.c. had been added, reacted only with the hydrogen-ions from the second stage, is shown by the variable values found for K_2. They, too, increased to about 9×10^{-5}. The falling-off of the values of K_2 towards the end of the titration
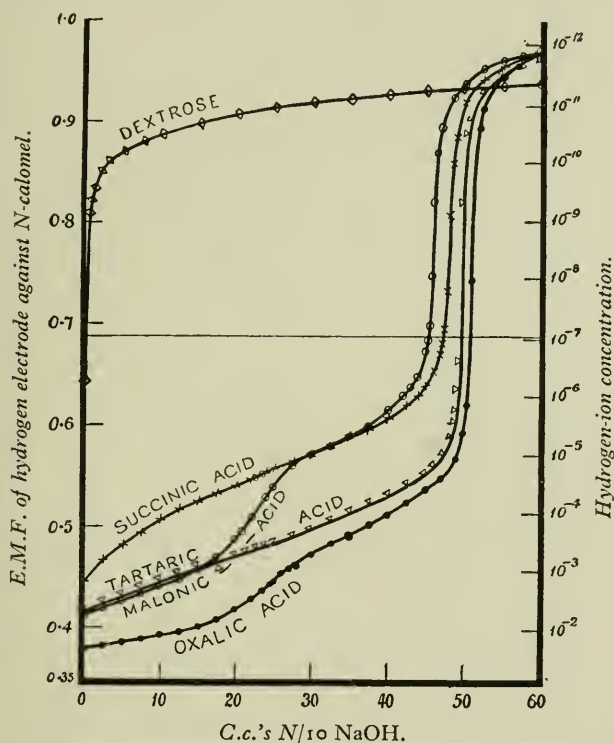

FIG. 42.—Hydrogen Electrode Titration Curves of Dibasic Acids and of Dextrose :—100 c.c. of (i) 0·0255 M.-Oxalic acid, (ii) 0·0250 M.-Tartaric acid, (iii) 0·0240 M.-Succinic acid, (iv) 0·0230 M.-Malonic acid, and 140 c.c. of 0·3572 M.-Dextrose.

are probably to be accounted for by the fact that the solution was then undergoing a rapid change in pH, thus causing very small inaccuracies in reading the voltages lead to comparatively large errors in K_2. Hence, Table 27 shows that no constancy in the values of K_1 and K_2 is obtained, except perhaps for those values calculated from voltages indicated at the beginning and towards the end of the titration.

TABLE 27.

TITRATION OF 100 C.C. OF 0·0250 M.-TARTARIC ACID WITH 0·100 N-NaOH at 18°.

C.c. of NaOH.	E.M.F. against N-calomel —Volt.	pH.	Conc. of Free Tartaric Acid × 10^3.	a.	[H_2T] × 10^2.	[HT'] × 10^3.	K_1 × 10^3.
0	0·415	2·29	25·0	0·206	19·9	—	1·34
2·5	0·423	2·43	22·0	0·170	18·3	6·18	1·27
5·0	0·430	2·55	19·0	0·149	16·2	7·60	1·33
7·5	0·437	2·67	16·3	0·132	14·1	9·29	1·41
10·0	0·444	2·79	13·6	0·119	12·0	10·7	1·45
12·5	0·450	2·89	11·1	0·115	9·8	13·4	1·61
15·0	0·457	3·02	8·70	0·111	7·7	14·0	1·75
17·5	0·463	3·12	6·38	0·119	5·6	15·7	2·11
20·0	0·470	3·24	4·17	0·138	3·6	17·2	2·76
21·25	0·473	3·29	3·09	0·164	—	—	—
22·5	0·477	3·36	2·04	0·213	—	—	—
23·75	0·480	3·41	1·01	0·382	—	—	—
25·0	0·4835	3·474	—	—	—	—	—
					Na_2T.	NaHT.	K_2 × 10^3.
27·5	0·490	3·59	—	—	2·5	22·5	2·87
30·0	0·496	3·69	—	—	5·0	20·0	5·08
32·5	0·506	3·87	—	—	7·5	17·5	5·85
35·0	0·514	4·00	—	—	10·0	15·0	6·62
37·5	0·523	4·16	—	—	12·5	12·5	6·92
40·0	0·529	4·26	—	—	15·0	10·0	8·19
42·55	0·540	4·45	—	—	17·55	7·45	8·30
45·0	0·551	4·64	—	—	20·0	5·0	9·08
46·25	0·559	4·78	—	—	21·25	3·75	9·35
47·5	0·571	4·99	—	—	22·5	2·5	9·19
48·5	0·587	5·27	—	—	23·5	1·5	8·43
49·0	0·604	5·56	—	—	24·0	1·0	6·56
49·25	0·616	5·77	—	—	24·25	0·75	5·48
49·5	0·637	6·14	—	—	24·5	0·5	3·59
49·75	0·664	6·60	—	—	24·75	0·25	2·47
50·0	0·822	9·34	—	—	—	—	—
50·5	0·884	10·42	—	—	—	—	—
51·0	0·901	10·71	—	—	—	—	—
52·5	0·928	11·18	—	—	—	—	—
55·0	0·945	11·48	—	—	—	—	—
57·5	0·956	11·66	—	—	—	—	—
60·0	0·961	11·75	—	—	—	—	—

Calculation of the Dissociation Constants of Dibasic Acids from Titration Curves.

The following equations are based on the mass law and apply to solutions which are so dilute that the sodium salts may be taken as completely dissociated.

Let c = the total concentration of acid, a = total concentration of added alkali, and h = hydrogen-ion concentration. A dibasic acid, H_2R, dissociates thus :

$$\text{(i) } H_2R \rightleftharpoons H^{\boldsymbol{\cdot}} + HR' \quad \text{(ii) } HR' \rightleftharpoons H^{\boldsymbol{\cdot}} + R'',$$
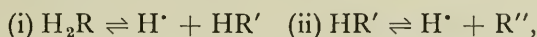
such that $K_1 = h[HR']/[H_2R]$ and $K_2 = h[R'']/[HR']$. Then $[H_2R] + [HR'] + [R''] = c$ and in the case of the neutralisation of the majority of dibasic acids, excepting those which are extremely weak and for ion-concentrations prevailing towards the end of the neutralisation of fairly weak acids,

$$H^{\boldsymbol{\cdot}} + Na^{\boldsymbol{\cdot}} = HR' + R''$$
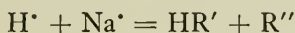
whence
$$a + h = [HR'] + 2[R''] \text{ (Case I.)}.$$

In the case of extremely weak acids and during the final stage of neutralisation of fairly weak acids hydrolysis comes into play and the hydroxyl-ion concentrations so introduced must then be taken into account, then

$$H^{\boldsymbol{\cdot}} + Na^{\boldsymbol{\cdot}} = HR' + R'' + OH'$$

and
$$a + h = [HR'] + 2[R''] + \overline{oh}$$
$$\text{(Case II.} : \overline{oh} = [OH]).$$

Case I.

By eliminating the three unknown concentrations $[H_2R]$, $[HR']$ and $[R'']$ from the first four equations, we obtain the equation

$$\frac{a + h}{h + 2K_2} = \frac{cK_1}{h^2 + hK_1 + K_1K_2}$$

and $\therefore$.

$$K_1 = h^2(a + h)/\{K_2(2c - a - h) - (ah + h^2 - hc)\} \quad . \quad (1)$$
$$K_2 = \{h^2(a + h) + K_1(ah + h^2 - hc)\}/K_1(2c - a - h) \quad . \quad (2)$$

Putting

$$a_nh_n + h_n{}^2 - h_nc_n = A_n, \quad 2c_n - a_n - h_n = B_n,$$

and
$$h_n{}^2(a_n + h_n) = D_n,$$

then

$$K_1 = D_n/(K_2B_n - A_n) \text{ and } K_2 = (D_n + K_1A_n)/K_1B_n.$$

Hence, by taking any two points on the titration curve whose parameters are respectively A_1, B_1, D_1, and A_2, B_2, D_2, the values of K_1 and K_2 can be found.

Thus

$$K_1 = (B_1D_2 - B_2D_1)/(A_1B_2 - A_2B_1) \qquad . \qquad . \quad (3)$$
$$K_2 = (A_1D_2 - A_2D_1)/(B_1D_2 - B_2D_1) \qquad . \qquad . \quad (4)$$

Many of the values of K_2 for dibasic acids have hitherto been obtained from determinations of the hydrogen-ion concentrations of solutions of the acid salts and calculated by means of a formula, worked out by Noyes (*Z. physikal. Chem.*, 1893, **11**, 495), identical with (2), for when $a = c$, as is the case with an acid salt, NaHR, the equation becomes

$$K_2 = h^2(c + K_1 + h)/K_1 \, (c - h) \qquad . \qquad . \quad (5)$$

Case II.

Elimination of the three unknowns $[H_2R]$, $[HR']$ and $[R'']$ from the first three fundamental equations and the equation involving $\overline{oh}$, we obtain the expression

$$\frac{a + h - \overline{oh}}{h + 2K_2} = \frac{cK_1}{h^2 + hK_1 + K_1K_2},$$

from which it follows that

$$K_1 = h^2(a + h - \overline{oh})/\{K_2(2c - a - h + \overline{oh}) \\ - (ah + h^2 - hc - h \cdot \overline{oh})\}$$

and

$$K_2 = \{h^2(a + h - \overline{oh}) + K_1(ah + h^2 - hc \\ - h \cdot \overline{oh})\}/K_1(2c - a - h + \overline{oh}).$$

In Table 28 the values of K_1 and K_2 as calculated from the titration data of tartaric acid, Table 27, by means of the formulæ derived on page 151, are compared with the values given in Table 27, which were obtained from the data corresponding to the same positions on the curve. The values of K_1 and K_2 calculated from the formulæ are much more satisfactory than those based on the assumption that the second hydrogen-ion does not react until the first equivalent of alkali has been added, provided that the pairs of points employed for the calculation are not taken at either of the ends of the titration curve. The last two sets of values gave absurd results of the particular constant which at that stage of the neutralisation was not then being involved. These values are given in brackets. That the second dissociation came into play during the neutralisation of the first 15 c.c. of NaOH (= 0·6 equivalent) will be evident from the satisfactory value of K_2 calculated from the two points o and 15.

TABLE 28.

CALCULATION OF K_1 AND K_2 FROM TITRATION CURVE.
DISSOCIATION CONSTANTS OF TARTARIC ACID.

C.c. of NaOH.	$K_1 \times 10^3$.		$K_2 \times 10^5$.	
	Formula.	Table.	Formula.	Table.
5 } 45 }	1·22	1·33	9·56	9·08
10 } 40 }	1·24	1·45	9·30	8·19
15 } 35 }	1·30	1·75	8·56	6·62
20 } 30 }	1·22	2·76	10·61	5·08
0 } 25 }	1·28	1·34	9·68	—
5 } 30 }	1·21	1·33	10·65	5·08
0 } 15 }	1·29	{ 1·34 { 1·75	9·16	—
20 } 30 }	1·29	—	9·64	—
0 } 5 }	1·35	{ 1·33 { 1·27	[− 1·24]	—
40 } 50 }	[0·91]	—	9·65	{ 8·19 { 9·08
Mean 1·27		—	9·65	—

Hydrogen-Ion Concentration at Half-Neutralisation of a Dibasic Acid.

If it happens that the two stages of ionisation of a dibasic acid, H_2R, are similar to those of weak monobasic acids, then for

$$H_2R \rightleftharpoons H^{\cdot} + HR'$$

$$K_1 = \frac{[H^{\cdot}][HR']}{[H_2R]} = [H^{\cdot}] \times \frac{[\text{acid salt}]}{[\text{acid}]}$$

and   for $$HR' \rightleftharpoons H^{\cdot} + R'$$

$$K_2 = \frac{[H^{\cdot}][R']}{[HR']} = [H^{\cdot}] \frac{[\text{neutral salt}]}{[\text{acid salt}]}.$$

Now suppose that when 1 equivalent of NaOH had been added a fraction of an equivalent, β, of the hydrogen-ions arising from the first stage of ionisation failed to react, and consequently β equivalent of NaOH must have reacted with the hydrogen-ions produced by

the subsequent ionisation of HR' ions. If c is the original concentration of H_2R, then the NaHR formed will be $(1 - \beta)c$ and the concentration of Na_2R will be βc. The concentration of undissociated acid, $[H_2R]$, will be βc. Substituting these values in the above expressions, we get

$$K_1 = [H^\bullet] \times \frac{(1 - \beta)c}{\beta c},$$

and

$$K_2 = [H^\bullet] \times \frac{\beta c}{(1 - \beta)c},$$

whence by multiplication, we find that

$$K_1 \times K_2 = [H^\bullet]^2,$$

or

$$p\mathrm{H} = \frac{p\mathrm{K}_1 + p\mathrm{K}_2}{2}.$$

Thus, provided that both stages of a dibasic acid are weak, the pH at the mid-point of its neutralisation is equal to the mean of the exponents, $p\mathrm{K}_1$ and $p\mathrm{K}_2$. These for weak monobasic acids are equal to the pH of the hydrogen-ion concentrations prevailing at their half-neutralisation, and, in fact, they are true for the separate stages of a dibasic acid, for as a general rule up to the point corresponding to the addition of the first half an equivalent of alkali the hydrogen-ion concentration is uninfluenced by K_2, and later during the addition of the final half equivalent K_1 becomes ineffective.

The identity, $K_1 K_2 = [H^\bullet]^2$, may also be derived from Noyes' formula, connecting K_1 and K_2 with the hydrogen-ion concentration of solutions of acid salts, NaHR, and proved on page 152. As $K_2 = h^2(c + K_1 + h)/K_1(c - h)$ we find that the condition that

$$K_1 . K_2 = h^2$$

is that

$$\frac{c + K_1 + h}{c - h}$$

must be equal to unity. This can only be true when both K_1 and h are negligibly small compared with the concentration, c. Such conditions hold when the first stage of dissociation is governed by a constant not greater than 10^{-3}. This will be seen from Table 29, in which $p\mathrm{H}_M$ corresponds to the hydrogen-ion concentration at the mid-point of neutralisation of each of the four acids given in Fig. 42. The figures in the last column are the values assumed by

$$\frac{c + K_1 + h}{c - h} = \frac{K_1 . K_2}{[H^\bullet]_M^2}$$

for the various acids. With the exception of oxalic acid, in which case the first stage is that of a fairly strong acid the value of this expression is approximately 1, so much so that pH_M and

$$\frac{pK_1 + pK_2}{2}$$

are in fair accord.

TABLE 29.

RELATIONSHIP BETWEEN THE HYDROGEN-ION CONCENTRATION AT HALF-NEUTRALISATION AND THE DISSOCIATION CONSTANTS OF DIBASIC ACIDS.

Acid.	$pH_M.$	$pK_1.$	$pK_2.$	$\dfrac{pK_1 + pK_2}{2}.$	$\dfrac{K_1 . K_2}{[H^{.}]_M^2}$
Oxalic . . .	2·88	0·77	3·86	2·32	13·0
Tartaric . . .	3·47	2·90	4·02	3·46	1·09
Succinic . . .	4·73	4·04	5·28	4·66	1·42
Malonic . . .	4·11	2·70	5·36	4·03	1·45

By an approximate mathematical analysis Auerbach and Smolczyk have shown how the character of the titration curves is determined by the ratio of their dissociation constants. Thus when K_1 is greater than $16K_2$ the curve will have an inflexion in the middle, whereas when $K_1 = 16K_2$ the curve will be a straight line, and when K_1 is less than $16K_2$ the curve will be similar to that of a monobasic acid. The curves of oxalic and malonic acids, the second dissociation constants of which are considerably less than $1/16K_1$, viz., $1/1269$ and $1/476$ respectively, have each large inflexions (Fig. 42), whereas in that of succinic acid ($K_1 = 17K_2$) and of tartaric acid ($K_1 = 13K_2$) no inflexions are discernible.

It is striking that the first two members—oxalic acid and malonic acid—of the saturated dibasic acid series,

$$HO_2C . [CH_2]_n . CO_2H,$$
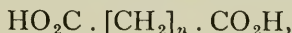
should exhibit such a great difference in their two dissociation constants, in each case the first constant being several hundred times the second, as compared with the next member, succinic acid, the first constant of which is only seventeen times the second. The dissociation constants found by Chandler (*J. Amer. Chem. Soc.*, 1908, **30**, 713) for the remaining members of the series up to sebacic acid, $n = 8$, reveal the remarkable fact that the values of K_2 from malonic acid upwards are all approximately equal and

of the order 10^{-6}, and that there is only a small diminution in K_1 of the ascending acids of the series, but they are all of the order given by succinic acid, $viz.$, 10^{-5}. Hence the titration curves of these acids will be similar to that of succinic acid, and, in fact, almost coincident with it.

The views relating to the acidity of dibasic acids held at the present time appear to be those which were first enunciated by Ostwald (*Z. physikal. Chem.*, 1892, **9**, 553) and are based on the electrostatic charges carried by the various ions and the influence that may be exerted by virtue of the proximity of the carboxyl groups. He considered that in the ionisation of a dicarboxylic acid the negative charge carried by the anion, arising from the first dissociation, exerted a force of repulsion on the negative charge carried by the other carboxyl group and that the nearer one carboxyl group was to the other the greater would be this repulsive force, which would therefore tend to prevent the ionisation proceeding to the second stage.

FIG. 43.—Analysis for Titration Curves.

The examples which Ostwald gave were those of fumaric and maleic acids and thus the hypothesis gave excellent support to the van't Hoff theory accounting for their structure. The hypothesis does not, however, obtain such a marked success when applied to the series in question. It does seem to hold when applied to the first two acids—oxalic and malonic—but it is difficult to see why the interposition of a further methylene group in the case of succinic acid should have such a considerable effect in making

K_1 approach K_2 in magnitude. It would have been expected, moreover, that as the chain of methylene groups became longer and longer and the repulsive force between the negative charges held by the carboxyl groups grew less and less, the second stage of dissociation would have become greater and greater, gradually becoming equal to the very slowly decreasing K_1, instead of remaining unchanged. (See, however, Bjerrum, *Z. physikal. Chem.*, 1923, **106**, 238.)

The neutralisation curves of polybasic acids or polyacidic bases are composed essentially of the curves corresponding to each separate stage of ionisation. Provided the acid or base is not too strong, we have seen that the midpoint of each integral curve will pass through a pH equal to pK_a or, in the case of bases, equal to $pK_w - pK_b$. In Figs. 43 and 44 the theoretical neutralisation curves of the

FIG. 44.—Analysis for Titration Curves.

first and second stages of some dibasic acids have been inserted as broken lines. Whereas in the chromic acid curve the two stages of neutralisation are distinct from one another, the theoretical lines being coincident with the two branches, we find that if the first stage of malonic acid were uninfluenced towards the end of its neutralisation, the reaction would be completed at about pH 4·8, and the second hydrogen-ion would come into action at about pH 3·3 and the pH change would follow the broken line to approximately the mid-point of the second half of the curve. Such a state of affairs would, of course, be impossible, and consequently we see from the actual curve that neither of

these pH values are attained but that the hydrogen-ion concentrations indicated refer to intermediate pH values. The actual curve is tangential to the two monobasic branches. The proximity of the two constants, compared with those of chromic acid, leads to a less well-defined inflexion. In Fig. 43, the inflexion is seen to be less for ortho-phthalic acid, of which $K_1 = 150\ K_2$. We also see from the positions where the observed curve becomes tangential to the constituent curves why ionisation of the second stage becomes involved early during the addition of the first half of alkali and why hydrogen-ions arising from the first stage are not completely used up until considerably more than one equivalent of alkali has been added. This is greater with tartaric and succinic acids whose respective constants are much closer together, pK$_2$ — pK$_1$ being slightly greater than 1. It therefore becomes evident why the pH curves corresponding to the middle stages of their neutralisation should be rectilinear and give no evidence of inflexions, as mentioned above. A glance of the three constants of citric acid given in Table 21 will reveal that no very pronounced inflexions can occur in its pH curve. As the difference between pK$_2$ and pK$_1$ is 1·6, a very small inflexion will be produced on the addition of the first equivalent of alkali, whereas pK$_3$ — pK$_2$ being 1·2 the inflexion at the end of the second stage will be imperceptible. It is for this reason that citric acid and its salts are often included in buffer solutions.

Potentiometric Estimation of Acids and Bases which are too weak to be estimated volumetrically.

Harris (*Proc. Roy. Soc.*, 1923, B, **95**, 440 ; *J. Chem. Soc.*, 1923, **123**, 3294) has recently developed a method for the estimation of very weak acids and bases, similar to that previously employed by Tague (*J. Amer. Chem. Soc.*, 1920, **42**, 180) in connexion with work on certain ampholytes of importance in the chemistry of flour. Incidentally, it is the same in principle as that employed for the calculation of the dissociation constants of weak acids (and bases), which on treatment with alkali (or acid) gives rise to salts which are considerably hydrolysed (*cf.* p. 129). It was shown that for an acid whose degree of dissociation α is negligibly small $K_a = [H^{\cdot}] \times \dfrac{[\text{salt}]}{[\text{acid}]}$, and similarly for a base $K_b = [OH']$ $\times \dfrac{[\text{salt}]}{[\text{base}]}$. In the case of moderately weak acids and bases the salt formed, *i.e.*, [salt], was equivalent to the titrant added, but for extremely weak acids and bases this is far from being the case.

The " salt " concentration can be calculated from the amount of titrant added and the hydrogen-ion concentration, for the latter concentration is set up solely by the amount of titrant which has failed to react.   Hence by knowing the degree of dissociation of the titrant when in the concentration indicated by the pH it is an easy matter to calculate how many cubic centimetres had actually failed to react, which when subtracted from the amount of titrant actually added, gives the amount which has combined with the acid or base.   The amount of titrant, alkali or acid, may, of course, be ascertained directly by merely adding it to water, until the pH, produced in the actual titration, is attained, and finding by simple proportion the amount required for the particular volume of the titrated solution.   Harris, however, realised that for an acid or base of which its affinity constant was known, neutralisation, within experimental error, must take place between two definite pH's. These could be calculated by taking the ratio of [salt]/[acid], (or [base]), at the beginning of a titration was 1/99, and at the end 99/1 respectively.

Thus, as shown on page 131, at the beginning of the titration of an acid $K_a = [H^{\cdot}]_1 \times \dfrac{1}{99}$, and at the end $K_a = [H^{\cdot}]_2 \times \dfrac{99}{1}$, and therefore

$$[H^{\cdot}]_1 = 99 \times 99 \text{ times } [H^{\cdot}]_2$$
$$= 10{,}000 \text{ times } [H^{\cdot}]_2,$$

approx., or $pH_1 = pH_2 - 4$.   In other words, the pH interval between the beginning and end of a titration is 4.   Similarly for bases, $pOH'_1 = pOH'_2 - 4$, or $pH^{\cdot}_1 = pH^{\cdot}_2 + 4$, for $pOH' = pK_w - pH^{\cdot} = 14 - pH^{\cdot}$.   Hence, the limits of pH prevailing during the neutralisation of a weak acid by a strong alkali $pK_a \mp 2$, and similarly the pH limits between which weak bases are neutralised by strong acids are $14 - pK_b \pm 2$.   For glycine, $K_a = 1 \cdot 8 \times 10^{-10}$, and therefore, when the acid is 1 per cent. neutralised the pH is $7 \cdot 75$, and when 99 per cent. neutralised it is $11 \cdot 75$. The basic dissociation constant K_b of glycine is $2 \cdot 7 \times 10^{-12}$, and, therefore, the pH at beginning of neutralisation with hydrochloric acid is $4 \cdot 43$ and $0 \cdot 43$ at the end (actually 99 per cent. neutralised).   It is, therefore, only necessary to titrate between these limits, and by ascertaining the amount of free reactant the amount neutralised by the acid or base is known.   Fig. 45 gives the pH curves, constructed from the data of Tague and Harris which represent potentiometric titrations of glycine when treated with alkali, and also when treated with an acid, from which the true neutralisation curves were obtained by deducting the amounts
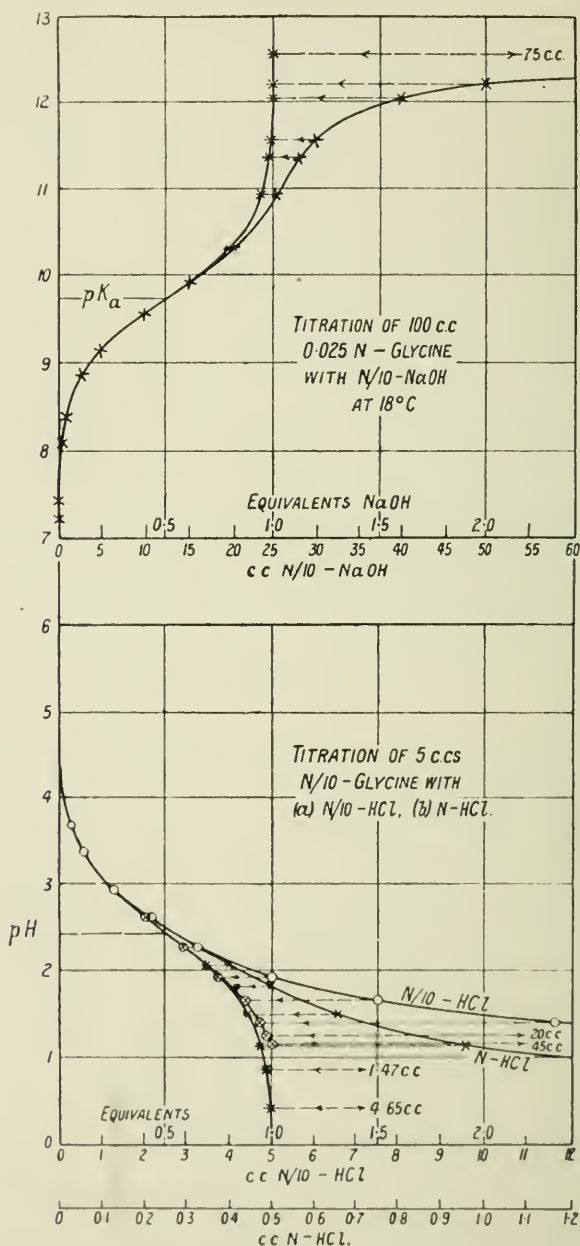
FIG. 45.—Potentiometric Titrations of Glycine with Sodium Hydroxide and Hydrochloric Acid.

unreacted upon, and which gave rise to the pH from the various additions of titrant.

Titration of Glutamic Acid.

Harris (*J. Chem. Soc.*, 1923, **123**, 3299) has titrated glutamic acid hydrochloride by means of the quinhydrone electrode. As will be seen from Table 24 this acid is an ampholyte and contains two carboxyl groups and one amino-group. Moreover, the values of the affinity constants of the two acid groups are widely different, *viz.*, $6 \cdot 2 \times 10^{-5}$ and $1 \cdot 6 \times 10^{-10}$, and thus the pH ranges of neutralisation of the two stages will be quite distinct. The weaker group will enter into reaction between pH 7·8 and 11·8, and the stronger between pH 2·21 and 6·21. The dissociation constant of the basic group being $1 \cdot 3 \times 10^{-12}$ will cause its neutralisation to take place between pOH 9·9

FIG. 46.—Titration of Glutamic Acid Hydrochloride.

and 13·9, or as $K_w = 10^{-14}$ between pH 4·1 and 0·1. It appears therefore that the neutralisation of the stronger acid group and the basic group will take place within the pH range covered by the quinhydrone electrode. Furthermore, the pH of a solution of glutamic acid will be determined by some kind of compensation of the stronger acid group and the basic group. The continuous curve in Fig. 46 represents the pH change undergone when 20 c.c. of a decimolar solution of glutamic acid hydrochloride were titrated with decinormal alkali. In order to estimate the glutamic

acid we see from the foregoing that it will be necessary to find the exact amount of sodium hydroxide which reacts only with the unhydrolysed hydrochloride in the first place, and with the stronger carboxyl group in the second. These two reactions take place between pH o·1 and pH 6·21. Owing to the considerable hydrolysis of the glutamic hydrochloride, resort must be made to the procedure adopted in the case of glycine to find the amount of hydrochloric acid, in terms of c.c. of N/10—HCl for each particular volume of solution, corresponding to the hydrolysed acid and indicated by the pH after each addition of alkali. In this way the " ideal curve of neutralisation of the
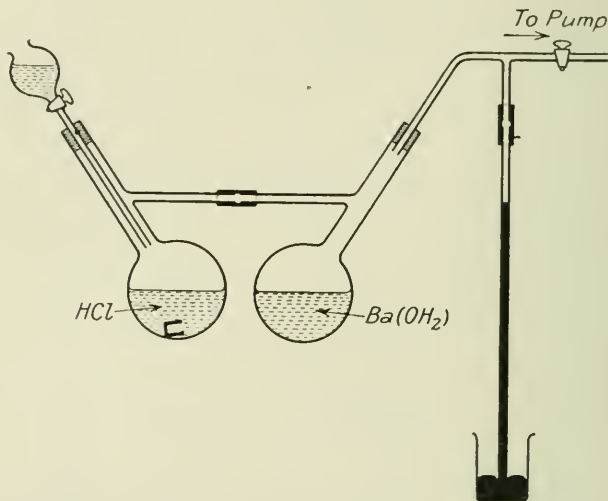
FIG. 47.—Apparatus for the Estimation of Carbon Dioxide.

glutamic acid hydrochloride," shown in Fig. 46 as a broken line, can be constructed. The curve shows that 40 c.c. of NaOH were required. This so-called " ideal curve " is actually that of the amino-group, which on neutralisation with N/10 — HCl would have followed the course from the 20 c.c. abscissa to the left. The broken lines in the middle of the curve refer to the base and acid in the absence of one or the other. The very small inflexion of the actual curve illustrates the effect of the two constants.

Baryta Vacuum Method of Estimating Carbon Dioxide.

This method depends upon the absorption of carbon dioxide by a saturated solution of baryta, neutralising the excess of barium

hydroxide by bringing the solution to the phenolphthalein end-point, then adding an excess of a standard solution of an acid and returning to the methyl orange end-point with standard alkali. The curves given in Fig. 47 illustrate the principle upon which the method is based, for which the author is indebted to Mr. F. J. Watson, M.A., M.Sc., of Melbourne, and also for the following particulars. The apparatus required is shown in Fig. 47.

The carbonate sample is weighed out in a small glass capsule, which may be made from a test-tube, and is dropped into the distilling flask on the left. An excess of saturated barium hydroxide solution is put in the other flask. If the percentage of CO_2 in the sample is known approximately the necessary volume of $Ba(OH)_2$ to provide an excess is readily calculated. The system is then evacuated by the pump, which is preferably a Gaede, but may be a good jet pump. The system is isolated from the pump by the tap and the mainten-

FIG. 48.—Principle of Estimating Carbon Dioxide.

ance of the vacuum checked by the mercury gauge. Dilute HCl is cautiously admitted from the tap funnel and the flask on the right shaken to absorb the CO_2 as evolved. The bottom of the first flask is now heated directly with a small Bunsen flame and the distillation continued vigorously for at least 5 minutes. The vacuum is now broken by opening the tap of the tap funnel, and the $Ba(OH)_2$, $BaCO_3$ mixture in the second is rapidly titrated with standard HCl to the phenol-phthalein end-point. (If this end-point is over-shot return

quickly with NaOH before any CO_2 is lost.) If the volume and normality of the original $Ba(OH)_2$ is known this titre will give a measure of the CO_2 absorbed, but in most cases it is not used. A slight excess of the standard HCl over that required to dissolve the carbonate is now added, and the excess back-titrated with standard NaOH to the methyl orange end-point. It is not practicable to titrate the $BaCO_3$ directly as its reaction with the acid is too slow where the excess of acid is very small in the vicinity of the end-point.

Curve I in Fig. 48 refers to the titration of a solution of barium hydroxide containing suspended barium carbonate. The broken line gives the approximate course taken by the pH of the solution, exact values not being possible on account of the evolution of carbon dioxide which was taking place. The dissolution of the barium carbonate is indicated by a downward inflexion and may be detected with methyl orange, though preferably the exact end-point should be judged by comparison with the colour produced in a solution buffered at about pH 4·5. Curve II is the back-titration curve with NaOH of a solution containing an excess of free acid after CO_2 has been expelled by boiling. As may be seen from the great inflexion thereby obtained, such a titration will lead to more satisfactory results.

Abnormal Acids.

Certain acids, such as silicic and tungstic, which are insoluble in aqueous solution, undergo anomalous changes in hydrogen-ion concentration in the process of neutralisation. We shall here refer to the two acids mentioned in regard to their volumetric estimation.

Silicic Acid.

Although the reaction of silicic acid with alkalis has received some study in recent years by measurements of the hydrogen-ion concentrations of solutions of silicic acid in sodium hydroxide (Bogue, *J. Amer. Chem. Soc.*, 1920, **42**, 2575 ; Joseph and Oakley, *J. Chem. Soc.*, 1925, **127**, 2814 ; Harman, *J. Physical Chem.*, 1926, **30**, 1100 ; Hägg, *Z. anorg. Chem.*, 1926, **155**, 20), there still remains much uncertainty as to the actual manner in which the acid ionises, and, moreover, the results hitherto recorded do not give a complete account of the variation in hydrogen-ion concentration throughout the course of neutralisation at 18°. Hägg states that, if silicic acid is not colloidal, K_1 of metasilicic acid is of the order of 10^{-9} and K_2 about 10^{-13}. The curve given in Fig. 91 on page 414 shows the change in hydrogen-ion concentration when 100 c.c. of a

solution 0·0929 N with respect to NaOH and 0·0224 M. with respect to SiO_2, were titrated at 18° with 0·0973 N-hydrochloric acid. The ratios of Na_2O to SiO_2 present in the solution at the different stages of neutralisation are indicated on the curve. Two inflexions occurred in that portion corresponding to the addition of 2 equivs. of sodium hydroxide to 1 mol. of silicic acid, and the point corresponding to half-neutralisation of metasilicic acid, *i.e.*, $Na_2O,2SiO_2$, lies just at the beginning of the second inflexion at pH 10·4. As other workers have shown, the ionisation of silicic acid cannot be represented satisfactorily in terms of two dissociation constants ; moreover, the titration curve is not typical of a dibasic acid inasmuch as when K_1 and K_2 are widely different the point corresponding to half-neutralisation should lie somewhere about the middle of the second inflexion—in Fig. 91 it should be near the point corresponding to pH 11. The curve, however, shows that silicic acid enters into some kind of combination with sodium hydroxide, and it gives some idea of the hydrogen-ion concentrations that are thereby set up. It also shows that the hydrogen-ion concentration imparted by silicic acid to a solution is much too small to have any effect on the methyl orange end-point, and hence the reason why the alkali present in a silicate solution may be titrated by using such an indicator.

Tungstic Acid.

The facts that tungstic oxide forms salts with the alkali metals, R_2WO_4, and that tungsten appears in the same group of the periodic system as sulphur have led to the impression that tungstic acid is an ordinary dibasic acid. The author (*J. Chem. Soc.*, 1927, 148) has made a preliminary study of the oxide by following electrometrically the variation in hydrogen-ion concentration during the course of its neutralisation with sodium hydroxide ; for this purpose, however, he found it more convenient to back-titrate a solution of the oxide in sodium hydroxide with hydrochloric acid. The first portion of the titration curve, given in Fig. 49, was constructed from E.M.F. measurements at 20° made between a hydrogen electrode immersed in the solution and a normal calomel half-element, the junction liquid being a saturated solution of potassium chloride. The P.D's were reproducible until pH 4 was reached, when the hydrogen in the electrode began to reduce catalytically the sexavalent tungsten to the quinquevalent state, as indicated by the appearance of the characteristic blue coloration around the electrode. This position is denoted by R on the curve. The three points on the diagram obtained after reduction became

obvious represent initial readings made before the effect of the reduction had become appreciable. To complete the titration curve, resort was had to the oxygen electrode, with which a similar titration was carried out using solutions of the same concentrations. Neither the hydrogen-electrode nor the oxygen-electrode curve showed that any abrupt changes in hydrogen-ion concentration occurred in solutions more acidic than pH 4. The remaining portion of the curve in Fig. 49 was plotted from the oxygen electrode curve, calibrated against the portion obtained with the
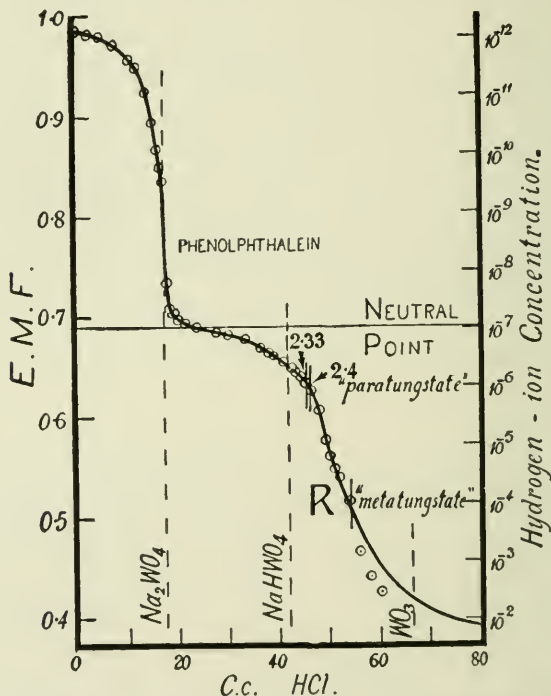
FIG. 49.—Electrometric Titration of a Solution of NaOH and Na_2WO_4 with HCl.

hydrogen electrode, the accuracy of which is considered to be of the order of one-tenth of a pH unit. The curve given in Fig. 49 represents the titration by 0·1020 N-hydrochloric acid of 100 c.c. of a solution which was 0·0678 N with respect to sodium hydroxide and 0·0250 M. with respect to tungstic acid (WO_3).

The curve shows that a sharp diminution in pH took place with the amount of hydrochloric acid necessary to react with the alkali in excess of that required to form the normal sodium tungstate. This explains why tungstic acid may be estimated volu-

metrically either by titrating a suspension of it directly with sodium hydroxide or by dissolving the oxide in alkali and titrating the excess of alkali with acid, using in each case phenolphthalein as indicator (Hundeshagen, *Chem.-Ztg.*, 1894, **18**, 547 ; Herting, *Z. angew. Chem.*, 1901, **14**, 165 ; Lind and Trueblood, *J. Amer. Chem. Soc.*, 1907, **29**, 477).   The remaining part of the curve down to the dotted line indicating WO_3 represents, in effect, the reverse of the neutralisation of tungstic acid with sodium hydroxide.   The large inflexion produced when the acid was about one-quarter neutralised is surprising in that it did not occur when the acid was half-neutralised, as would have been the case had tungstic acid behaved as an ordinary dibasic acid with widely differing dissociation constants.

No precipitation of tungstic oxide occurred throughout the titration even although a large excess of hydrochloric acid had been added.   The solution remained perfectly clear.   Using more concentrated solutions, precipitation ensues (see van Liempt, *Z. anorg. Chem.*, 1923, **127**, 215 ; *Rec. trav. chim.*, 1924, **43**, 30).

The curve throws some light on the so-called " paratungstates " and " metatungstates."   Sodium paratungstate is stated to have the composition $3Na_2O,7WO_3,21H_2O$ or $5Na_2O,12WO_3,28H_2O$, and thus it contains either 2·33 or 2·4 mols. of Na_2O to 1 mol. of WO_3.   The points on the titration curve marked 2·33 and 2·4 indicate the hydrogen-ion concentrations of the solutions when the solutes were present in those ratios, the pH being 6·1 and 6·0, respectively.   Schmidt (*Amer. Chem. J.*, 1886, **8**, 16) found that a solution of the 2·4 salt was acidic to rosolic acid and alkaline to cochineal ; consequently the pH of his solution was in the neighbourhood of 6, and was therefore in accord with the value indicated by the curve.   The point marked " metatungstate " gives the hydrogen-ion concentration, 10^{-4}, of the solution when the alkali in combination with the tungstic acid was that required by $Na_2W_4O_{13}$, the formula given to sodium metatungstate.   Although the hydrogen-ion concentrations of the " para " and " meta " solutions show that some kind of union took place, it is difficult to picture the exact nature of that union.   It appears from the curve that the paratungstate solution is the same as that of a solution of sodium tungstate saturated with tungstic oxide in such a way that the change in hydrogen-ion concentration undergone is very small, whereas the metatungstate solution corresponds to a still greater saturation, but one which involves a considerable variation in hydrogen-ion concentration.   These are the conditions which underlie the preparation of these salts.   Seeing that tungstic acid cannot be considered as an ordinary dibasic acid, it is not apparent what kind

of compounds these are, unless it be supposed that they contain tungstic acid either in a polymerised form or in a semi-colloidal form.

Quinhydrone electrode titration curves of molybdic acid reveal that it dissociates in a very similar manner to tungstic acid.

We shall now consider the mathematical relationships involved in the hydrolysis of salt solutions and in the ionisation of ampholytes.
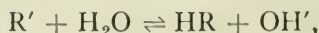
Hydrolysis.

It is well known that very few salts when dissolved in water produce solutions which are neutral in reaction. Some of the base in the case of a salt formed from a strong base and a weak acid breaks away and imparts to the solution an alkaline reaction, whereas an acidic reaction is established by a salt composed of a strong acid and a weak base. If both the acid and the base from which the salt was formed happen to be soluble in water, then it becomes possible to calculate the hydrolysis constant of such hydrolytic reactions and the pH values of the resulting solutions.

(a) Hydrolysis of a Salt of a Strong Base and a Weak Acid (*e.g.*, Sodium acetate).

Consider the reaction

$$BR + H_2O \rightleftharpoons HR + BOH.$$
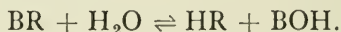
If the salt, BR, be in dilute solution, we may assume that that portion of it which has not suffered hydrolysis will be almost completely ionised into B˙ and R′ ions. For the purpose of calculation we shall regard it as complete. The base, BOH, is a strong one, so that its ionisation will also be taken as complete. The acid, HR, is a weak one and its dissociation, $HR \rightleftharpoons H˙ + R′$, is so very small, which coupled with the relatively large concentration of hydroxyl-ions cause the hydrogen-ions produced by it to have no measurable effect upon the reaction of the solution. The hydrolytic action might therefore be re-written

$$R′ + H_2O \rightleftharpoons HR + OH′,$$

the kations, B˙, through the assumed complete ionisation of BR, taking no part. On applying the mass law, we find that

$$K_{\text{hydrolysis}} = \frac{[HR][OH′]}{[R′]}.$$

Multiplying numerator and denominator by [H'], and knowing that

$$K_w = [H^\cdot][OH'],$$

and

$$K_a = [H^\cdot][R']/[HR],$$

we obtain

$$K_{hydrolysis} = \frac{[HR]}{[H^\cdot][R']} \times [H^\cdot][OH'],$$

$$\frac{K_w}{K_a}$$

i.e.,

$$K_{hydrolysis} = \frac{K_w}{K_a}.$$

We are now in a position to obtain an approximate expression connecting the pH of a solution of BR, K_w and the dissociation constant of HR, *viz.*, K_a. We may assume if *the amount of hydrolysis be very small* that the concentration, c, of the salt, BR, = [R'], and as [HR] = [OH'], then

$$\frac{[HR][OH']}{[R']} = \frac{[OH']^2}{c} = \frac{K_w}{K_a},$$

$$\therefore [OH'] = \sqrt{\frac{K_w}{K_a} \times c},$$

whence

$$p\text{OH} = \tfrac{1}{2}\,p\text{K}_w - \tfrac{1}{2}\,p\text{K}_a - \tfrac{1}{2}\log c$$

and therefore

$$p\text{H} = \tfrac{1}{2}\,p\text{K}_w + \tfrac{1}{2}\,p\text{K}_a + \tfrac{1}{2}\log c.$$

The degree of hydrolysis of such a salt is equal to $[OH']/c$, and the percentage hydrolysis by $[OH'] \times 100/c$.

(b) **Hydrolysis of a Salt of a Weak Base and a Strong Acid** (*e.g.*, Ammonium chloride). In this case HR is strong and BOH weak, and the hydrolytic reaction will be

$$B^\cdot + H_2O \rightleftharpoons BOH + H^\cdot,$$
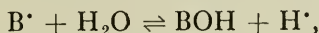
the R'-ions taking no part in the reaction as both the salt and strong acid are strongly ionised, and are here assumed to be ionised completely. As above

$$K_{hydrolysis} = \frac{[BOH][H^\cdot]}{[B^\cdot]} = \frac{[BOH]}{[B^\cdot][OH']} \times [H^\cdot][OH']$$

$$= \frac{K_w}{K_b},$$

where K_b is the affinity constant of the base, BOH. Also

$$\frac{K_w}{K_b} = \frac{[H^\cdot]^2}{c},$$

for $[H^\cdot] = [BOH]$ and $c = [B^\cdot]$. Therefore

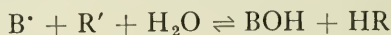$$[H^\cdot] = \sqrt{\frac{K_w}{K_b}} \times c.$$

and consequently,

$$pH = \tfrac{1}{2}\,pK_w - \tfrac{1}{2}\,pK_b - \tfrac{1}{2}\log c.$$

The percentage degree of hydrolysis

$$= [H^\cdot] \times 100/c.$$

(c) **Hydrolysis of a Salt of a Weak Base and a Weak Acid** (*e.g.*, Ammonium acetate). Here, both the ions, $B^\cdot$ and R', constituting the salt BR, which is taken as completely dissociated, are free to enter into combination with the few hydrogen- and hydroxyl-ions dissociated from the water to form undissociated base, BOH, and the undissociated acid, HR, by virtue of their weakness. The reaction is therefore

$$B^\cdot + R' + H_2O \rightleftharpoons BOH + HR$$

and
$$\begin{aligned}
K_{hydrolysis} &= \frac{[BOH][HR]}{[B^\cdot][R']} \\
&= \frac{[BOH]}{[B^\cdot][OH']} \times \frac{[HR]}{[H^\cdot][R']} \times [H^\cdot][OH'] \\
&= \frac{K_w}{K_b \cdot K_a}.
\end{aligned}$$

Now
$$[BOH] = [HR],$$

and
$$[B^\cdot] = [R'] = c, \text{ the concentration of the salt.}$$

Hence
$$\frac{K_w}{K_b \cdot K_a} = \frac{[BOH][HR]}{[B^\cdot][R']} = \frac{[HR]^2}{c^2},$$

but
$$K_a = \frac{[H^\cdot][R']}{[HR]} = \frac{[H^\cdot] \cdot c}{[HR]},$$

therefore
$$\frac{[HR]^2}{c^2} = \frac{[H^\cdot]^2}{K_a^2} = \frac{K_w}{K_b \cdot K_a},$$

$$\therefore [H^\cdot] = \sqrt{\frac{K_w \cdot K_a}{K_b}},$$

and, finally
$$pH = \tfrac{1}{2}\,pK_w + \tfrac{1}{2}\,pK_a - \tfrac{1}{2}\,pK_b.$$

The percentage degree of hydrolysis is $[HR] \times 100/c$ which may be evaluated from the foregoing expressions.

We observe from the above theoretical considerations that in the cases (a) and (b) the pH of the salt solutions is linked up with the concentration of the salt dissolved, but that in the last case (c) the pH is independent of the salt concentration. The formulæ lead to pH values which are in good agreement with those practically determined.

pH Value of Solutions of Ampholytes.

Ampholytes are those substances which have the power of reacting either as an acid or a base. As a rule their basic and acidic functions are weak and can only be brought effectively into action by means of strong acids and bases respectively. Examples are to be found amongst the carbon compounds and the inorganic compounds, such as glycine, the proteins, and hydrated alumina Amphoteric bodies like the proteins and certain inorganic hydroxides do not always pass into true solution, and their behaviour is thereby rendered more difficult to study through their colloidal nature. In those cases, it is probable that the reactivity and the pH imparted to the aqueous medium are the result of interfacial equilibria of ionic micelles. The isoelectric point of an ampholyte corresponds to a state of affairs when the ampholyte is at its minimum chemical activity, and it therefore exists in solution or in pseudo-solution, in its maximum undissociated condition. This causes colloidal bodies, e.g., gelatin, to acquire its minimum solubility, and inter-related with it are such physical properties as changes in the viscosity of their hydrosols, and in the swelling of their gels, which then acquire minimum values. The main factor which determines the isoelectric point is the pH of the mother-liquor. At pH values below that of the isoelectric point the colloidal particles bear positive charges, for under the influence of an electric field they migrate towards the cathode, whereas at pH values above that of the isoelectric point the particles assume a negative charge and move in the opposite direction. At the isoelectric point they behave as if they were without an electric charge for they remain stationary when a current is passed through the solution. Actually, the particles are in a state of electrical neutrality. Expressed in purely chemical terms, this means that in acid solutions of hydrogen-ion concentration greater than that indicated by the isoelectric point pH the colloidal particles are basic in nature, whereas at smaller hydrion concentrations they
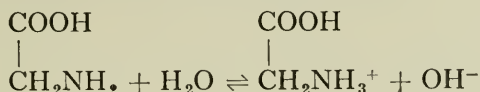
behave as if they were acids and react with alkalis. Thus an ampholyte will be in the isoelectric condition when no part of it is in combination with any acid or alkali. In the case of an ampholyte which is a distinct chemical individual, *e.g.*, glycine, it is customary to refer to this condition merely in terms of the hydrogen-ion concentration which it establishes in its solution, and to confine the term, isoelectric point, to the complex colloidal amphoteric bodies.
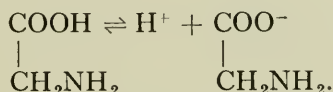
We shall now evaluate the pH value of a solution of a simple ampholyte in terms of the affinity constants of the acid and basic groups. We see from Fig. 45 that the amino-group in glycine reacts with acid below pH 6, whereas above this pH it reacts with alkali apparently through interaction with the carboxyl-group. Because of the great difference between the two pH ranges within which these groups enter into reaction, it follows that at pH about 6 the amount of combination with either of these groups will be immeasurably small. This, however, is not true for such ampholytes as *m*-aminobenzoic acid and aspartic acid. The values given in Table 24 show that *m*-aminobenzoic acid reacts as an acid between pH 2·8 and pH 6·8, and as a base between pH 0·1 and pH 4·1. These two ranges overlap and consequently whilst only the basic function is reacted upon from pH 0·1, the acid function comes into play at pH 2·8 before the neutralisation of the basic group is complete. The titration curve is similar to that of glutamic acid, Fig. 46. The behaviour of aspartic acid is similar. It is evident, then, that the pH of a solution of an ampholyte will be dependent upon the affinity constants of the basic and acidic groups, for their magnitude will determine whether any interaction will take place between these groups and so set up a state of partial mutual neutralisation. There are two ways of regarding the behaviour of ampholytes : (i) to assume that a molecule may behave either as if it were a base alone or as an acid, *i.e.*, once the -NH$_2$ group has entered into reaction the -COOH becomes incapacitated and *vice versâ ;* (ii) to assume that the carboxyl- and the amino-groups of a molecule of an ampholyte have interacted to form an " inner salt," which may be decomposed either by an acid or an alkali. In the latter case, one part of the molecule behaves as an anion, *i.e.*, negatively charged, and the other part as a cation, positively charged. A doubly ionised molecule is a so-called " hybrid ion " or a " Zwitterion." This is *Bjerrum's Theory* (*Z. physikal. Chem.*, 1923, **104,** 147), and the mathematical consequences will be dealt with subsequently.

We shall now consider the pH value of a solution of an

ampholyte in terms of the first conception. Thus glycine may react in accordance with either the dissociation,

$$\begin{array}{cc} \text{COOH} & \text{COOH} \\ | & | \\ \text{CH}_2\text{NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{NH}_3{}^+ + \text{OH}^- \end{array}$$

or the dissociation,

$$\begin{array}{cc} \text{COOH} \rightleftharpoons \text{H}^+ + \text{COO}^- \\ | \qquad\qquad | \\ \text{CH}_2\text{NH}_2 \qquad \text{CH}_2\text{NH}_2. \end{array}$$

Let [A] represent the concentration of undissociated ampholyte in either of the two modes of ionisation, [A˙] the concentration of basic ions (cations) and [A′] the concentration of anions. Hence in the general case

$$A + H_2O \rightleftharpoons A^{\cdot} + OH'$$

and

$$A \qquad\qquad \rightleftharpoons H^{\cdot} + A'.$$
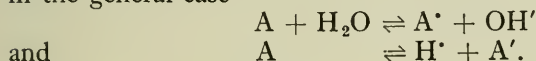
For the basic dissociation,

$$K_b = \frac{[A^{\cdot}][OH']}{[A]},$$

and for the acidic dissociation,

$$K_a = \frac{[H^{\cdot}][A']}{[A]}.$$

Because of the electrical neutrality of the solution, we can write

$$[A^{\cdot}] + [H^{\cdot}] = [OH'] + [A'].$$

By substituting $\dfrac{K_w}{[H^{\cdot}]}$ for [OH′],

$$\frac{K_b \cdot [A][H^{\cdot}]}{K_w} \text{ for } [A^{\cdot}], \text{ and}$$

$$\frac{K_a \cdot [A]}{[H^{\cdot}]} \text{ for } [A']$$

in the above equation, and solving for [H˙], we obtain the following relationsip :—

$$[H^{\cdot}] = \sqrt{\frac{K_a \cdot [A] + K_w}{\dfrac{K_b}{K_w} \cdot [A] + 1}}.$$

This expression gives the hydrogen-ion concentration of an ampholyte in terms of the several constants and the unknown concentration, [A]. If, as we have seen, the *p*H titration ranges of the

acidic and basic groups are sufficiently well apart as is the case with glycine, then the concentration of the undissociated ampholyte will be equal to the concentration of the ampholyte, c, so that $[A] = c$. In the other cases referred to on page 172 there will be appreciable concentrations of $A^{\cdot}$ and A', and then the equality

$$c = [A] + [A^{\cdot}] + [A']$$

must be taken into consideration. For such ampholytes Kolthoff (*Indicators*, Kolthoff, translated by Furman, New York, 1926, p. 44) has shown that if as a first approximation $[A]$ is assumed equal to c, an approximate estimate of $[H^{\cdot}]$ may be obtained which when substituted in the equation

$$[A^{\cdot}] + [H^{\cdot}] = [OH'] + [A']$$

will give an equation which when solved for $[A^{\cdot}]$ and $[A']$ in conjunction with

$$[A^{\cdot}] + [A'] = -c - [A]$$

will lead to a more satisfactory value for $[A]$. By substituting this new value of $[A]$ in the original equation, a value of $[H^{\cdot}]$ will be obtained which may be regarded as accurate. The following Table, No. 30, gives the results of Kolthoff's computations for aspartic acid, and were taken from his book :—

TABLE 30.

CALCULATION OF pH VALUES OF ASPARTIC ACID.

c.	pH.	pH Calculated *without* Correction.	pH Calculated *with* Correction.
1	2·95	2·95	2·95
10^{-1}	2·97	2·97	2·95
10^{-2}	3·11	3·08	2·97
10^{-3}	3·52	3·44	3·52
10^{-4}	4·17	3·91	4·17

If the values of K_a and K_b happen to be much greater than K_w, and not smaller than about 10^{-11}, and the concentration of undissociated ampholyte molecules, $[A]$, high, then we can write

$$[H^{\cdot}] = \sqrt{\frac{K_a \cdot [A] + K_w}{\frac{K_b}{K_w} \cdot [A] + 1}} = \sqrt{\frac{K_a \cdot K_w}{K_b}}.$$

This expression is usually given for calculating the isoelectric point of proteins and of similar amphoteric substances. It should be mentioned, however, that the acid and basic functions of these bodies cannot satisfactorily represent in terms of dissociation constants (*cf.* Harris, *Proc. Roy. Soc.*, 1925, **97B,** 379).

Leonar Michaelis (*Hydrogen-Ion Concentrations*, translated by Perlzweig, 1927) obtains the expression in a somewhat different way. Substituting the values for [A$\cdot$] and [A$'$] given on page 173,

in
$$c = [A] + [A\cdot] + [A']$$

we get

$$\frac{c}{[A]} = 1 + \frac{K_a}{[H\cdot]} + \frac{K_b}{K_w} \cdot [H\cdot].$$

Differentiating, we obtain

$$\frac{d\left(\frac{1}{[A]}\right)}{d[H\cdot]} = -\frac{K_a}{[H\cdot]^2} + \frac{K_b}{K_w},$$

so that $\frac{1}{[A]}$ is at a minimum, when [A] is at a maximum, and this occurs when

$$-\frac{K_a}{[H\cdot]^2} + \frac{K_b}{K_w} = 0.$$

Hence at the isoelectric point

$$[H\cdot] = \sqrt{\frac{K_a K_w}{K_b}}.$$

It remains for us to discuss the ionisation of ampholytes on the basis of Bjerrum's " Zwitter " Ion Theory, according to which an ampholyte may dissociate in any of the ways shown by the following equations :—

$$NH_2 . R . COOH + H_2O = HO . NH_3 . R . COOH$$
$$\rightleftharpoons \overset{+}{N}H_3 . R . CO\overset{-}{O} + H_2O$$
$$\rightleftharpoons \overset{+}{N}H_3 . R . COOH + OH'$$
$$\rightleftharpoons HO . NH_3 . R . CO\overset{-}{O} + H\cdot.$$
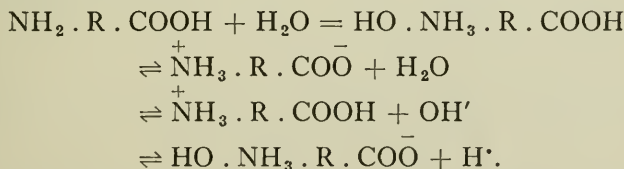
According to this scheme, we see that on solution there occurs a combination of the ampholyte with water molecules, molecule for molecule, and immediately followed by *either*, an internal neutralisation of the acid and basic groups, forming an electrically

neutral and undissociable " inner " salt, which therefore will be without effect on the conductivity of the solution and is known as the " Zwitter " ion or " hybrid-ion," *viz.*, $\overset{+}{N}H_3 . R . C\overset{-}{O}O$, *or* the formation of simple cations, $\overset{+}{N}H_3 . R . COOH$, *or*, of simple anions, $HO . NH_3 . R . C\overset{-}{O}O$.   On account of these equilibria it is unlikely that any undissociated ampholyte would remain as such in a solution, the solution being constituted of ions or " Zwitter " ions.

The acidic nature of the cations may be represented by the following reaction :—

$$\overset{+}{N}H_3 . R . COOH \rightleftharpoons \overset{+}{N}H_3 . R . C\overset{-}{O}O + H^{\cdot}$$
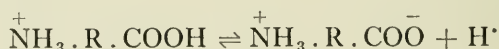
and the basic nature of the anions by

$$HO . NH_3 . R . C\overset{-}{O}O \rightleftharpoons OH' + \overset{+}{N}H_3 . R . C\overset{-}{O}O.$$
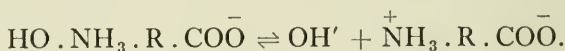
If we denote the " Zwitter " ion by Z, the cations, by $A^{\cdot}$, and the anions by A', these equations may be rewritten

$$A^{\cdot} \rightleftharpoons Z + H^{\cdot}$$
$$A' \rightleftharpoons OH' + Z.$$
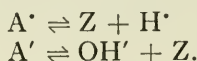
Hence, the acid ionisation will be governed by

$$\frac{[Z][H^{\cdot}]}{[A^{\cdot}]} = k_a$$

and the dissociation of the base, producing OH' ions, by

$$\frac{[OH'][Z]}{[A']} = k_b.$$

Bjerrum regards k_a and k_b as the *True Dissociation Constants* of the acidic and basic groups, whereas the constants K_a and K_b, previously discussed, are merely their *Apparent Constants*.

The concentration of the " Zwitter " ion, $[Z]$, of which the ampholyte in solution is chiefly composed, save for those concentrations which have entered into combination by virtue of either the acidic or basic groups, *viz.*, $[A^{\cdot}]$ and $[A']$, is clearly equal to the concentration of undissociated ampholyte when considered in terms of the first theory, i.e. $[Z] = [A]$.   If we multiply K_a by k_b we find that

$$K_a . k_b = \frac{[H^{\cdot}][A']}{[A]} \cdot \frac{[OH'][Z]}{[A']}$$

and therefore, Bjerrum's basic constant,

$$k_b = \frac{K_w}{K_a}.$$

Similarly Bjerrum's acidic constant,

$$k_a = \frac{K_w}{K_b}.$$

If Bjerrum's constants be compared with those derived on page 169 for the hydrolysis of salts, it will be observed that k_a is also the hydrolysis-constant of a salt formed from a weak base, whose dissociation constant is K_b, and a strong acid, and that k_b is the hydrolysis-constant of a salt obtained from a strong base and a weak acid having a constant, K_a. In other words, Bjerrum's constant, k_a, refers to the hydrolytic action by means of hydrogen-ions of the carboxyl-end of the "Zwitter" ion. Thus the action of hydrochloric acid might be represented thus :
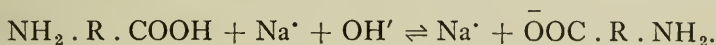
$$\overset{-}{O}OC . R . \overset{+}{N}H_3 + H^{\cdot} + Cl' \rightleftharpoons HOOC . R . \overset{+}{N}H_3 + Cl'$$
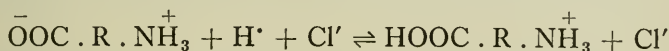
whereas, according to the first theory, such a reaction is essentially that of the neutralisation of a base, thus :

$$HOOC . R . NH_2 + H^{\cdot} + Cl' \rightleftharpoons HOOC . R . \overset{+}{N}H_3 + Cl'$$
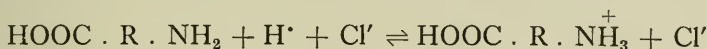
and is consequently controlled by K_b. Likewise k_b refers to the hydrolysis of the "Zwitter" ion to form the anion carrying the free base thus :

$$\overset{-}{O}OC . R . \overset{+}{N}H_3 + Na^{\cdot} + OH' \rightleftharpoons Na^{\cdot} + \overset{-}{O}OC . R . NH_3OH$$
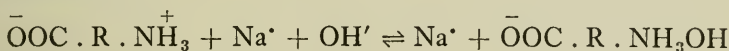
and K_a to the analogous reaction

$$NH_2 . R . COOH + Na^{\cdot} + OH' \rightleftharpoons Na^{\cdot} + \overset{-}{O}OC . R . NH_2.$$

For these reasons the "Zwitter" ion theory provides a satisfactory explanation of the mode of dissociation of ampholytes and accounts equally well as the previously described theory for the titration curves obtained.

If Bjerrum's concept be the true one then it appears that instead of amino-acids containing very weak acidic and basic groups they must contain groups which have comparatively strong acidic and basic properties which cause the basic and acidic

groups to interact with one another to form stable " Zwitter " ions. Thus we have seen that the ordinary constants of glycine are

$$K_a = 10^{-9.7} \text{ and } K_b = 10^{-11.6},$$

whereas by taking $K_w = 10^{-14}$ it follows that Bjerrum's corresponding constants are

$$k_b = 10^{-4.3} \text{ and } k_a = 10^{-2.4} \text{ respectively.}$$

The lower curve in Fig. 45 showing the action of hydrochloric acid would therefore correspond to the hydrolysing action of the " Zwitter " ion by the acid in liberating the ampholyte acid, of which $k_a = 10^{-2.4}$ and the upper curve corresponds to the opening-up of the " Zwitter " ion by the sodium hydroxide and setting free the ampholyte base, $k_b = 10^{-4.3}$. If this is actually the case then we see that Bjerrum's constants are indeed the true constants and the generally accepted constants apparent only. The theory appears to bring the strengths of acidic groups and basic groups contained in certain ampholytes into line with non-ampholyte acids and bases belonging to the different classes of derivatives.

Effect of Non-Aqueous Liquids on the Dissociation of Weak Bases.

Though comparatively little work has been done on the hydrogen-ion concentrations produced by acids and bases when neutralised in solutions comprising mixtures of water and organic liquids, e.g., alcohol and acetone, volumetric estimations are often performed in such media. These solvents may have pronounced effects on the colour changes of indicators and also on the dis-

TABLE 31.

DEPRESSING EFFECT OF ACETONE ON THE DISSOCIATION OF SOME WEAK ORGANIC BASES.

Solvent.	$p K_b$ in		
	Water.	50 Per Cent. Acetone. 50 Per Cent. Water.	90 Per Cent. Acetone. 10 Per Cent. Water.
Aniline	9·5	11·5	16·3
Methylaniline	9·3	11·5	16·0
Dimethylaniline	9·0	11·5	16·1
p-Nitroso-dimethylaniline	10·0	11·7	18·7
Glycine	11·5	12·5	—

sociation constants of the weak acids.   Hence the pH values corresponding to the equivalence-points will depend on the proportion of organic liquid in the solution.   Pring (*Trans. Faraday Soc.*, 1924, **19,** 705) has investigated the effect of acetone on the dissociation constants of a series of weak organic bases.   The neutral point varies with the composition of the solution.   Thus Pring found that $p\mathrm{K}_w$ of a solution of 50 per cent., by volume, of each acetone and water was 15·5, and 19·7 for a 90 per cent. acetone—10 per cent. water solution, compared with $p\mathrm{K}_w = 14\cdot1$ for pure water.   Hence, the neutral points occur at pH 7·75, 9·85 and 7·05 respectively.   The depressing effect of the non-aqueous solvent on the ionisation of some weak bases is shown in Table 31 in which is quoted some of the values obtained by Pring. The large increases in $p\mathrm{K}_b$ show that in every case the dissociation constants were diminished many-fold.

Further information relating to the use of indicators in volumetric analysis will be found on pp. 239-243.

CHAPTER XI.

SOLUTIONS OF KNOWN HYDROGEN-ION CONCENTRATIONS.

Standard Buffer Solutions.

SOLUTIONS which have definite hydrogen-ion concentrations, and which are buffered, are required in the colorimetric methods for the determination of pH values.   They are of service in bacteriological culture work and will very probably become of importance in analytical practice.   Such solutions constitute the basis of the greater part of colorimetric work, and for this reason several investigators have made very careful measurements of their hydrogen-ion concentrations by the standard electrical methods.   These standard buffer solutions thus provide a means by which the hydrogen-ion concentrations of unknown solutions are compared indirectly with the electromotive force data of the hydrogen electrode.   In the following tables are quoted data of solutions whose pH values extend from 0·6-12·0.   The data are based upon those obtained by Walpole (*Biochem. J.*, 1914, **105**, 2501, 2521), Sørensen (*Biochem. Z.*, 1909, **21**, 131 ; **22**, 352 ; *Ergebn. Physiol.*, 1912, **12**, 393), Clark and Lubs (*J. Bacteriol.*, 1917, **2**, 1, 109, 191), McIlvaine (*J. Biol. Chem.*, 1921, **49**, 183), Palitzsch (*Biochem. Z.*, 1915, **70**, 333), Ringer (cited by Kolthoff, " Indicators ") and Kolthoff (*J. Biol. Chem.*, 1925, **63**, 135).   Table 52 gives details of the " Universal Buffer Mixture " of Prideaux and Ward (*J. Chem. Soc.*, 1924, **125**, 426).

TABLE 32.

pH RANGE : 0·65–5·20 (WALPOLE).

50 c.c. N-Sodium Acetate + x c.c. N-HCl made up to 250 c.c.

pH		0·65	0·75	0·91	1·09	1·24	1·42	1·71
HCl (x)	.	100	90	80	70	65	60	55
pH	.	1·85	1·99	2·32	2·64	2·72	3·09	—
HCl (x)	.	53·5	52·5	51·0	50·0	49·75	48·5	—
pH	.	3·29	3·49	3·61	3·79	3·95	4·19	—
HCl (x)	.	47·5	46·25	45·0	42·5	40·0	35·0	—
pH	.	4·39	4·58	4·76	4·95	5·20	—	—
HCl (x)	.	30·0	25·0	20·0	15·0	10·0	—	—

TABLE 33.

pH RANGE : 1·00–2·20 (CLARK AND LUBS).

50 c.c. 0·2 M.-KCl + x c.c. 0·2 N-HCl made up to 200 c.c.

pH		1·0	1·2	1·4	1·6	1·8	2·0	2·2
HCl (x)		97·0	64·5	41·5	26·3	16·6	10·6	6·7

TABLE 34.

pH RANGE : 1·04–3·68 (SØRENSEN).

10 c.c. Mixtures of x c.c. of 0·1 M.-Glycine (0·1 M.-NaCl), and y c.c. of 0·1 M.-HCl.

pH		1·04	1·15	1·25	1·42	1·645	1·93
Glycine (x)		0·0	1·0	2·0	3·0	4·0	5·0
HCl (y)		10·0	9·0	8·0	7·0	6·0	5·0

pH		2·28	2·61	2·92	3·34	3·68	—
Glycine (x)		6·0	3·0	8·0	9·0	9·5	—
HCl (y)		4·0	3·0	2·0	1·0	0·5	—

TABLE 35.

pH RANGE : 1·04–4·96 (SØRENSEN).

10 c.c. Mixtures of x c.c. of 0·1 M.-Disodium Hydrogen Citrate and y c.c. of 0·1 M.-HCl.

pH		1·04	1·17	1·42	1·925	2·27	2·97
Citrate (x)		0·0	1·0	2·0	3·0	3·33	4·0
HCl (y)		10·0	9·0	8·0	7·0	6·67	6·0

pH		3·36	3·53	3·69	3·95	4·16	4·45
Citrate (x)		4·5	4·75	5·0	5·5	6·0	7·0
HCl (y)		5·5	5·25	5 0	4·5	4·0	3·0

pH		4·65	4·83	4·89	4·96	—	—
Citrate (x)		8·0	9·0	9·5	0	—	—
HCl (y)		2·0	1·0	0·5	10·0	—	—

TABLE 36.

pH RANGE : 2·2–3·8 (CLARK AND LUBS).

50 c.c. 0·1 M.-Potassium Biphthalate + x c.c. 0·1 N-HCl made up to 100 c.c.

pH		2·2	2·4	2·6	2·8	—
HCl (x)		46·70	39·60	32·95	26·42	—

pH		3·0	3·2	3·4	3·6	3·8
HCl (x)		20·32	14·70	9·90	5·97	2·63

TABLE 37.

pH RANGE: 2·2–8·0 (McIlvaine).

20 c.c. *Mixtures of x c.c. of* 0·2 $M.-Na_2HPO_4$ *and y c.c. of* 0·1 $M.-Citric\ Acid.$

pH	2·2	2·4	2·6	2·8	—	—
Na_2HPO_4 (x).	0·40	1·24	2·18	3·17	—	—
Citric acid (y)	19·60	18·76	17·82	16·83	—	—
pH	3·0	3·2	3·4	3·6	3·8	—
Na_2HPO_4 (x).	4·11	4·94	5·70	6·44	7·10	—
Citric acid (y)	15·89	15·06	14·30	13·56	12·90	—
pH	4·0	4·2	4·4	4·6	4·8	—
Na_2HPO_4 (x)	7·71	8·28	8·82	9·35	9·86	—
Citric acid (y)	12·29	11·72	11·18	10·65	10·14	—
pH	5·0	5·2	5·4	5·6	5·8	—
Na_2HPO_4 (x)	10·30	10·72	11·15	11·60	12·09	—
Citric acid (y)	9·70	9·28	8·85	8·40	7·91	—
pH	6·0	6·2	6·4	6·6	6·8	—
Na_2HPO_4 (x)	12·63	13·22	13·85	14·55	15·45	—
Citric acid (y)	7·37	6·78	6·15	5·45	4·55	—
pH	7·0	7·2	7·4	7·6	7·8	8·0
Na_2HPO_4 (x)	16·47	17·39	18·17	18·73	19·15	19·45
Citric acid (y)	3·53	2·61	1·83	1·27	0·85	0·55

TABLE 38.

pH RANGE: 3·0–5·8 (Kolthoff).

10 c.c. *Mixtures of x c.c.* 0·05 $M.-Succinic\ Acid\ and\ y\ c.c.$ 0·05 $M.-Borax.$

pH	3·0	3·2	3·4	3·6	3·8
Succinic acid (x)	9·86	9·65	9·40	9·05	8·63
Borax (y).	0·14	0·35	0·60	0·95	1·37
pH	4·0	4·2	4·4	4·6	4·8
Succinic acid (x)	8·22	7·78	7·38	7·00	6·05
Borax (y).	1·78	2·22	2·62	3·00	3·35
pH	5·0	5·2	5·4	5·6	5·8
Succinic acid (x)	6·32	6·05	5·79	5·57	5·40
Borax (y).	3·68	3·95	4·21	4·43	4·60

TABLE 39.

pH RANGE : 3·72–5·57 (WALPOLE).

10 c.c. Mixtures of x c.c. 0·2 N-Acetic Acid and y c.c. 0·2 N-Sodium Acetate.

pH		3·72	4·05	4·27	4·45	4·63
Acetic acid (x)		9·0	8·0	7·0	6·0	5·0
Sodium acetate (y)		1·0	2·0	3·0	4·0	5·0

pH		4·80	4·99	5·23	5·37	5·57
Acetic acid (x)		4·0	3·0	2·0	1·5	1·0
Sodium acetate (y)		6·0	7·0	8·0	8·5	9·0

TABLE 40.

pH RANGE : 4·0–6·2 (CLARK AND LUBS).

50 c.c. 0·1 M.-Potassium Biphthalate + x c.c. 0·1 N-NaOH made up to 100 c.c.

pH		4·0	4·2	4·4	4·6	4·8
NaOH (x)		0·40	3·70	7·50	12·15	17·70

pH		5·0	5·2	5·4	5·6	5·8
NaOH (x)		23·85	29·95	35·45	39·85	43·00

pH		6·0	6·2	—	—	—
NaOH (x)		45·45	47·00	—	—	—

TABLE 41.

pH RANGE : 4·96–6·33 (SØRENSEN).

10 c.c. Mixtures of x c.c. 0·1 M.-Disodium Hydrogen Citrate and y c.c. 0·1 N-NaOH.

pH		4·96	5·02	5·11	5·31	5·57	5·97	6·33
Citrate (x)		10·0	9·5	9·0	8·0	7·0	6·0	5·5
NaOH (y)		0·0	0·5	1·0	2·0	3·0	4·0	4·5
pH at 10° C.*.		4·93	4·99	5·08	5·27	5·53	5·97	6·30
pH at 40° C.*.		5·05	5·10	5·19	5·39	5·64	6·04	6·41

* Walbum, C.R. Soc. Biol., 1920, **83**, 707.

TABLE 42.

pH RANGE : 5·8–8·0 (CLARK AND LUBS).

50 c.c. 0·1 M.-K_2HPO_4 + x c.c. 0·1 M.-NaOH made up to 100 c.c.

pH		5·8	6·0	6·2	6·4	6·6	6·8
K_2HPO_4 (x)		3·72	5·70	8·60	12·60	17·80	23·65

pH		7·0	7·2	7·4	7·6	7·8	8·0
K_2HPO_4 (x)		29·63	35·00	39·50	42·80	45·20	46·80

TABLE 43.

pH RANGE : 5·8–9·2 (KOLTHOFF).

10 c.c. *Mixtures of x c.c. 0·1 M.-KH_2PO_4 and y c.c. 0·2 M.-Borax.*

pH	.	.	5·8	6·0	6·2	6·4	6·6	6·8
Phosphate (x)	.	9·21	8·77	8·30	7·78	7·22	6·67
Borax (y)	.	.	0·79	1·23	1·70	2·22	2·78	3·33

pH	.	.	—	7·0	7·2	7·4	7·6	7·8
Phosphate (x)	.	—	6·23	5·81	5·50	5·17	4·92
Borax (y)	.	.	—	3·77	4·19	4·50	5·83	5·08

pH	.	.	—	8·0	8·2	8·4	8·6	8·8
Phosphate (x)	.	—	4·65	4·30	3·87	3·40	2·76
Borax (y)	.	.	—	5·35	5·70	6·13	6·60	7·24

pH	.	.	—	9·0	9·2	—	—	—
Phosphate (x)	.	—	1·75	0·50	—	—	—
Borax (y)	.	.	—	8·25	9·50	—	—	—

TABLE 44.

pH RANGE : 5·91–8·04 (SϕRENSEN).

10 c.c. *Mixtures of x c.c. M./15-NaH_2PO_4 and y c.c. M./15-Na_2HPO_4.*

pH	.	.	5·91	6·24	6·47	6·64	6·81
NaH_2PO_4 (x)	.	9·0	8·0	7·0	6·0	5·0
Na_2HPO_4 (y)	.	1·0	2·0	3·0	4·0	5·0

pH	.	.	6·98	7·17	7·38	7·73	8·04
NaH_2PO_4 (x)	.	4·0	3·0	2·0	1·0	0·5
Na_2HPO_4 (y)	.	6·0	7·0	8·0	9·0	9·5

TABLE 45.

pH RANGE : 6·77–9·24 (PALITZSCH).

10 c.c. *Mixtures of x c.c. 0·2 M.-Boric Acid and y c.c. 0·05 M.-Borax.*

pH	.	.	6·77	7·09	7·36	7·60	7·78	7·94
Boric acid (x)	.	9·7	9·4	9·0	8·5	8·0	7·5
Borax (y)	.	.	0·3	0·6	1·0	1·5	2·0	2·5

pH	.	.	8·08	8·20	8·41	8·60	8·69	8·84
Boric acid (x)	.	7·0	6·5	5·5	4·5	4·0	3·0
Borax (y)	.	.	3·0	3·5	4·5	5·5	6·0	7·0

pH	.	.	8·98	9·11	9·24	—	—	—
Boric acid (x)	.	2·0	1·0	0·0	—	—	—
Borax (y)	.	.	8·0	9·0	10·0	—	—	—

TABLE 46.

pH RANGE : 7·62–9·24 (SØRENSEN).

10 c.c. Mixtures of x c.c. 0·05 M.-Borax and y c.c. 0·1 N-HCl.

pH	.	.	7·62	7·94	8·14	8·29	8·51	—	—
Borax (x)	.	5·25	5·5	5·75	6·0	6·5	—	—
HCl (y)	.	4·75	4·5	4·25	4·0	3·5	—	—
pH at 10° C.*	7·64	7·96	8·17	8·32	8·54	—	—
pH at 40° C.*	7·55	7·86	8·06	8·19	8·40	—	—

pH	.	.	8·68	8·80	8·91	9·01	9·09	9·17	9·24
Borax (x)	.	7·0	7·5	8·0	8·5	9·0	9·5	10·0
HCl (y)	.	3·0	2·5	2·0	1·5	1·0	0·5	0·0
pH at 10° C.*	8·72	8·84	8·96	9·06	9·14	9·22	9·30
pH at 40° C.*	8·56	8·67	8·77	8·86	8·94	9·01	9·08

TABLE 47.

pH RANGE : 7·81–10·0 (CLARK AND LUBS).

50 c.c. 0·1 M.-Boric Acid (0·1 M.-KCl) + x c.c. 0·1 N-NaOH made up to 100 c.c.

pH	.	7·8	8·0	8·2	8·4	8·6	8·8
NaOH (x)	2·61	3·97	5·90	8·50	12·00	16·30

pH	.	9·0	9·2	9·4	9·6	9·8	10·0
NaOH (x)	21·30	26·70	32·00	36·85	40·80	43·90

TABLE 48.

pH RANGE : 8·24–10·14 (SØRENSEN).

10 c.c. Mixtures of x c.c. 0·1 M.-Glycine (0·1 N-NaCl) and y c.c. 0·1 N-NaOH.

pH	.	.	8·24	8·58	8·93	9·36	9·71	10·14
Glycine (x)	.	9·75	9·5	9·0	8·0	7·0	6·0
NaOH (y)	.	0·25	0·5	1·0	2·0	3·0	4·0
pH at 10° C.*	—	8·75	9·10	9·54	9·90	10·34
pH at 40° C.*	—	8·12	8·45	8·85	9·18	9·58

TABLE 49.

pH RANGE : 9·24–9·97 (SØRENSEN).

10 c.c. Mixtures of x c.c. 0·05 M.-Borax and y c.c. 0·1 N-NaOH.

pH	.	.	.	9·24	9·36	9·50	9·68	9·97
Borax (x)	.	.	10·0	9·0	8·0	7·0	6·0
NaOH (y)	.	.	0·0	1·0	2·0	3·0	4·0
pH at 10° C.*	.	9·30	9·42	9·57	9·76	10·06
pH at 40° C.*	.	9·08	9·18	9·30	9·44	9·67

* Walbum

TABLE 50.

pH RANGE : 10·17–11·36 (KOLTHOFF).

50 c.c. 0·1 M.-Na_2CO_3 + x c.c. 0·1 N-HCl made up to 100 c.c.

pH	10·17	10·35	10·55	10·86	11·04	11·36
HCl (x)	20·0	15·0	10·0	5·0	3·0	0·0

TABLE 51.

pH RANGE : 10·97–12·06 (RINGER).

Add x c.c. 0·1 N-NaOH to 50 c.c. 0·15 M.-Na_2HPO_4.

pH	10·97	11·29	11·77	12·06
NaOH (x)	15·0	25·0	50·0	75·0

TABLE 52.

UNIVERSAL BUFFER MIXTURE (PRIDEAUX AND WARD).

pH RANGE : 2·0–11·8.

100 c.c. of a solution of mixed acids, being

> 0·04 M.-H_3PO_4,
> 0·04 N-Phenylacetic acid, and
> 0·04 N-Boric acid (HBO_2, H_2O),

neutralised with x c.c. of 0·2 N-NaOH, and made up to 200 c.c.
Interpolation Formula :—$pH = 0.773 + 0.1185\ x$ when x lies between 15 and 90 c.c.

pH	1·99	2·13	2·65	3·10	3·73
Per cent. neutralised	0	5·0	15·0	20·0	25·0
pH (calculated from formula)	—	—	2·55	3·14	3·74

pH	4·21	4·80	5·43	6·30	6·84
Per cent. neutralised	30·0	35·0	40·0	45·0	50·0
pH (calculated from formula)	4·33	4·91	5·51	6·11	6·70

pH	—	7·91	8·62	9·11	—
Per cent. neutralised	55·0	60·0	65·0	70·0	75·0
pH (calculated from formula)	7·28	7·88	8·48	9·07	9·66

pH	10·21	—	11·41	—	11·94
Per cent. neutralised	80·0	8·50	90·0	95·0	100·0
pH (calculated from formula)	10·25	10·85	11·45	—	—

N.B.—This mixture may also be prepared by substituting either potassium or sodium primary phosphate for the phosphoric acid, so as to make the buffer solution 0·04 Molar with respect to KH_2PO_4 or NaH_2PO_4. Such a solution on dilution from 100 c.c. to 200 c.c. will correspond in composition to that of the previous

buffer solution neutralised to the extent of 20 per cent. Its pH will therefore be 3·10, and on being neutralised will follow a linear relationship in pH until 90 per cent. of theoretical amount of alkali has been added. In the case of the modified buffer solution, this will correspond to the addition of 70 c.c. of 0·2 N-NaOH to 100 c.c. of the buffer solution and made up to 200 c.c. The interpolation formula will thus become

$$p\text{H} = 3\cdot10 + 0\cdot1185x.$$

Of these buffer mixtures all, with the exception of McIlvaine's disodium hydrogen phosphate-citric acid, Kolthoff's succinic acid-borax, and primary potassium phosphate-borax, and Prideaux and Ward's solutions, involve straightforward neutralisation reactions. The advantage accruing from the use of citric acid, which through the proximity of its three constants produces a uniform buffer action throughout the entire acid zone, in conjunction with sodium phosphate, Na_2HPO_4, involving phosphoric acid with its widely differing constants, is evident from the extensive pH range covered by McIlvaine's buffer solutions, $viz.$, pH 2-8. Kolthoff's two sets of solutions are important, in that they may be prepared by simply weighing out the pure substances and dissolving in the requisite amount of water, and also in the fact that the action of one set depends upon the interaction between two salts of acids having constants which lead to good buffer action, $viz.$, KH_2PO_4 and borax, and the other set between a dibasic acid, succinic, whose two constants are so close to one another that excellent buffer action results, and borax.

Prideaux and Ward's universal buffer mixture is simply a selection of acids whose dissociation constants differ from one another, when taken in turn, by a small ratio such that on neutralisation with alkali the pH-alkali curve is approximately rectilinear. We saw on page 155 that if K_1 of a dibasic acid is not greater than 16 times K_2 no inflexion in the pH curve is obtained and the curve is perfectly straight. Greater ratios of $K_1 : K_2$ will lead to inflexions, though as may be seen from Fig. 50 the inflexion is not considerable in the case of o-phthalic acid of which $K_1 = 150$ times K_2. The universal buffer mixtures, being made up of equivalent proportions of phenylacetic acid and boric acid and an equimolecular proportion of phosphoric acid may be regarded as a pentabasic acid whose constants, given as exponents, are successively

pK$_1$ = 2·0 (H_3PO_4, 1st stage), pK$_2$ = 4·3 (phenylacetic acid),
    pK$_3$ = 6·9 (H_3PO_4, 2nd stage), pK$_4$ = 9·2 (HBO_2),
and pK$_5$ = 11·6 (H_3PO_4, 3rd stage).

Prideaux and Ward's intention appears to have been to prepare a mixture whose buffer action towards NaOH might be represented as a rectilinear pH curve. If each succeeding pair of constants bore to one another the ideal relationship for this condition to hold, the first constant should not be greater than 17 times the second. As the logarithm of 17 is 1·23, it follows that this should be the maximum increment in the increasing pK values. The differences between the exponents of the several constants given
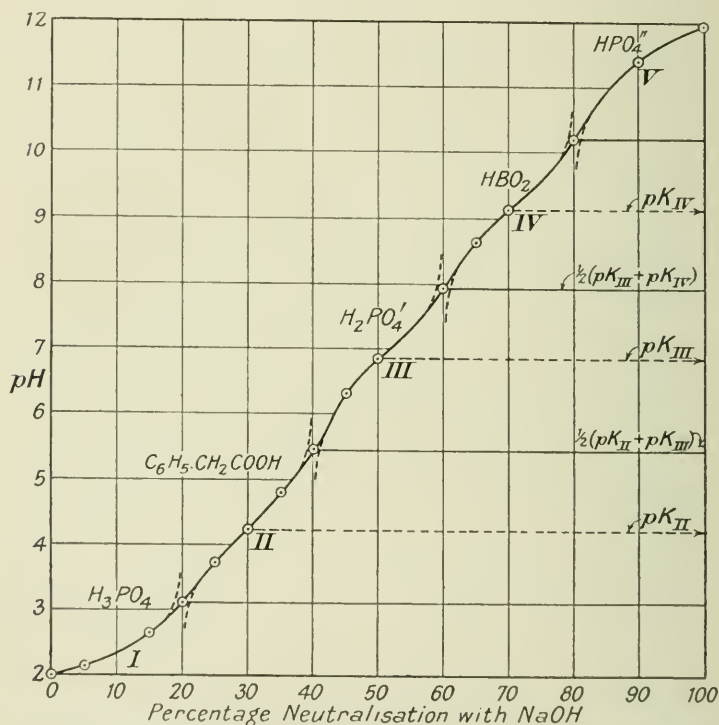
FIG. 50.—Percentage Neutralisation with NaOH. Prideaux and Ward's Universal Buffer Mixture.

above are 2·3, 2·6, 2·3 and 2·4, and as these are each greater than 1·2, the appearance of the many small inflexions are thus explained (Fig. 50). This has been made clearer in the figure by showing the separate monobasic acid titration curves, partly as broken lines. The curve of the buffer mixture is tangential to the separate constituent curves and incorporates just those sections which exhibit the more uniform buffer action. The horizontal lines drawn from the curve to the right-hand ordinate illustrate the approxi-

mate relationship, which we found on page 155, to exist between the exponents of the various constants of a mixture of acids at the apparent beginning and ending of the neutralisation of each individual acid.

As regards a buffer mixture covering the acid zone, it is probable that a more satisfactory mixture would comprise phosphoric and citric acids, whose constants as exponents are 2·0, 3·0, 4·6, 5·8, 6·9 when considered in the order of neutralisation with alkali. No inflexions would therefore be produced and when taken over short intervals the *p*H curve would be rectilinear.

Thus we see that the acids selected for use in the various standard buffer mixtures are of gradually increasing weakness, and the solutions advocated for use as standards are composed of them in varying degrees of neutralisation.   Only those solutions are chosen which on slightly altering their composition undergo a small change in *p*H, for obviously a solution whose buffer capacity is small is of little use as a standard.   It might be argued that such a range of solutions is unnecessary, for solutions can readily be prepared having any desired *p*H with a suitable acid whose dissociation constant is accurately known.   Though the latter procedure may lead to satisfactory standards for approximate colorimetric work, and is indeed advocated by one distinguished worker in this field, it is probably better and certainly more convenient to use solutions which have been accurately standardised directly against the hydrogen electrode.

If satisfactory standards are to be prepared every care must be taken to use pure materials, and in this respect the following notes may be of assistance.

Sodium Hydroxide.

Perhaps the most important solution, and incidentally the most troublesome to prepare, is that of sodium hydroxide, in that it should be free from carbonate.   For ordinary purposes, however, absolute freedom is unnecessary, and the method adopted by Sørensen might be employed.   A good sample of sodium hydroxide, *e.g.*, one prepared from sodium, or purified with alcohol, is dissolved in water, about 100 grams of alkali to 120 c.c. water.   This solution is placed in a tall stoppered cylinder and the impurities mainly carbonate, allowed to settle out by leaving the cylinder standing for a couple of days.   After the decantation of clear liquid and filtration through glass wool, the solution which is about 17N, is diluted to the required concentration.   The diluted alkali solution should be tested for any carbonate by carefully

adding hydrochloric acid to a portion until the pink colour produced by phenolphthalein is just on the point of disappearing. This will cause any carbonate to be converted into bicarbonate, whose presence may be detected by adding a neutral solution of barium chloride. If the colour fades then bicarbonate may be taken as present.

The sodium hydroxide solution may be standardised against either hydrochloric acid, or a solution of benzoic acid, prepared from the pure crystals, or as suggested by Dodge (*J. Ind. Eng. Chem.*, 1915, **7**, 29) against a solution of carefully purified potassium hydrogen phthalate (see p. 191).

Other methods are available for the preparation of carbon dioxide-free sodium hydroxide. One is to cover some cooled boiled-out water with a layer of ether, and to introduce into the mixture freshly cut pellets of sodium. These will float on the surface of the water and so interact. The ethereal layer will prevent the ingress of carbon dioxide. Afterwards the ether is expelled by boiling. Another method is to suspend some bright sodium in a nickel or silver gauze cage above a beaker placed inside a bell-jar and to lead in steam. A concentrated alkali solution will result. Much care is necessary to suck out the hydrogen that is liberated, not to allow any appreciable pressure to be set up within the bell-jar and to avoid too rapid attack of the steam such as may result from the sudden fall of a little condensed water on to the sodium. This method has been known to end in disaster.

The most satisfactory method is to prepare sodium amalgam electrolytically and to run it into CO_2—free water. This may be carried out in a separating funnel. Redistilled mercury is placed in the bottom, above which is a saturated solution of pure sodium chloride. Electrolysis is effected by means of two or three 2-volt accumulators placed in series. The mercury is made the cathode by connecting the negative pole to it by a wire dipping into a mercury contact placed in a closed glass tube, passing through the end of which is a platinum wire whose other end is completely immersed in the mercury, and the anode is a platinum wire. As the electrolysis proceeds shaking may be necessary to prevent the crystallisation of the amalgam. When sufficient amalgam is formed, the current is stopped, and the amalgam cautiously dropped into water by opening the tap and placing the end of the tube below the level of the water.

Hydrochloric Acid.

The preparation of a solution of hydrochloric acid presents no difficulty. It may be standardised against sodium carbonate,

or may be standardised by preparation from a " constant-boiling " solution of hydrochloric acid (*cf.* Hulett and Bonner, *J. Amer. Chem. Soc.*, 1909, **31**, 390). Under an atmospheric pressure of 760 mm. of mercury this solution boils at 108·5° C., and at 15° C. contains 20·242 per cent. HCl by weight. To prepare a decinormal solution it is necessary to take 18·017 grams of the acid and make up to 1 litre.

Potassium Biphthalate.

This compound, which is used in some of Clark and Lubs' standard buffer solutions, may be prepared by Dodge's method (*loc. cit.*). Between 10 and 20 grams of orthophthalic acid, or a proportionally greater amount of phthalic anhydride, is dissolved in 100 c.c. of a concentrated potassium hydroxide solution (about 15 per cent.) and the *p*H of the resulting solution adjusted to that corresponding to a faint pink colour of phenolphthalein by the addition of just the necessary amount of acid or alkali. Boil and filter while hot. Set to crystallise and recrystallise twice from distilled water. The temperature at which crystallisation is allowed to take place must be above 20° C., for according to Dodge at lower temperatures a more acid phthalate separates out. The salt is rendered anhydrous by drying to constant weight at 110° to 115° C.

Phosphoric Acid and Alkali Metal Phosphates.

Primary and secondary orthophosphates appear in the standard mixtures, though in the opinion of the author it is more convenient to prepare suitable solutions of them by the partial neutralisation of phosphoric acid. Unless one is very fortunate, there is every likelihood that the primary and secondary products of commerce will be somewhat indefinite in composition, in regard to both the phosphate and water contents. The reason for this will be apparent from the results of D'Ans and Schreiner (*Z. physikal. Chem.*, 1910, **75**, 95) and of Parker (*J. Physical Chem.*, 1914, **8**, 653) of the appropriate Ternary Systems, *viz.*,

$$NaOH—H_3PO_4—H_2O,$$
and $$KOH—H_3PO_4—H_2O.$$

According to Sørensen, the primary potassium phosphate, KH_2PO_4, should be free from sulphate and chloride and when dried at 100° C. under 20 to 30 mm. pressure should not lose 0·1 per cent. of its weight, while on ignition the loss should be

13·23 per cent. The primary sodium salt is $NaH_2PO_4 . H_2O$ and if crystallised out below 10° C., $NaH_2PO_4, 2H_2O$. On drying at 100°, it yields the anhydrous salt. This salt may replace the potassium salt in the buffer mixtures without involving any error.

Sφrensen used a Kahlbaum preparation of disodium hydrogen phosphate corresponding to $Na_2HPO_4, 2H_2O$, and which when dried at 100° under 20 to 30 mm. pressure lost 25·28 ± 0·1 per cent. ; and 13·23 ± 0·1 on ignition. It may be as well to point out here that the hydration of this salt is dependent upon the temperature at which it is crystallised. It crystallises with 12 molecules of water below 36·5° C. ; above this temperature and below 48° C. with 7 ; between 48° and 95° with 2 ; while above 95°, in the anhydrous state. It is essential, therefore, that no calculations should ever be based upon any particular composition, unless it has been definitely ascertained.

Boric Acid and Borax.

Boric acid should be purified by recrystallisation, spread into thin layers and placed in a desiccator over fused calcium chloride until perfectly dry. It has the formula HBO_2, H_2O.

Borax, $Na_2B_4O_7, 10H_2O$, after the necessary recrystallisation should be dried to constant weight over deliquescent sodium bromide. One great advantage which attends the use of this salt lies in the fact that it can be accurately weighed. If, however, solutions of boric acid and sodium hydroxide whose concentrations are accurately known are available, solutions of borax can be readily prepared, for the composition of the solute is that of half-neutralised boric acid, $HBO_2 . H_2O$.

Sodium Carbonate.

This salt can easily be obtained by gently heating either sodium bicarbonate or sodium oxalate to constant weight. The salt should not be allowed to fuse and the temperature not to exceed 360° C.

Citric Acid. $H_3C_6H_5O_7 . H_2O$.

The water of crystallisation may be found by drying to constant weight at 70° and 20 to 30 mm. Loss in weight should be 8·58 ± 0·1 per cent.

Succinic Acid. $(CH_2 . COOH)_2$.

This acid contains no water of crystallisation and care must be taken not to form the anhydride by heating to too high a temperature. Solutions must be freshly made, for like those of tartaric and citric acids, it has a distinct tendency to become contaminated by mould formation, though to a great extent this may be prevented by adding a few drops of thymol without influencing the pH.

Glycine, Glycocoll, Amino-acetic Acid. $CH_2 . NH_2 . COOH$.

This compound appears in one of the Sørensen buffer solutions, but these particular solutions are rapidly becoming discontinued. Sørensen states that the solution obtained by dissolving 2 gms. in 20 c.c. of water should be clear and free from chloride and sulphate. Not more than 5 mgms. of ash should result from the ignition of 5 gms. of glycine, and the nitrogen constant found by the Kjeldahl method should be 18.68 ± 0.1 per cent.

Phenylacetic Acid. $C_6H_5 . CH_2COOH$.

Melting-point is 76° C.

CHAPTER XII.

COLORIMETRIC METHODS FOR THE DETERMINATION OF HYDROGEN-ION CONCENTRATIONS.

In order to obtain a working hypothesis of the principles underlying the estimation of pH values by observing the various colours and intensities of colour produced by indicators, we shall first of all briefly refer to some of the theories which have been advanced to account for the colour and the constitution of indicators in solutions of acid or alkaline reaction.

Theory of Indicators.

As the result of extensive studies on the changes of colour which many solutions undergo, Wilhelm Ostwald concluded that colour was inherently connected with the presence of ions, and that the colour of a solution was the direct effect of a coloured or colourless un-ionised compound and the different colours of the ions into which the compound may have dissociated. Thus, he considered indicators to be either weak acids or bases which may have one colour in the undissociated condition, and the anions, in the case of acids, and the cations, in the case of bases, to have a different colour. If we denote an indicator which is a weak acid by HIn, and a weak base indicator by InOH, then we may represent their colour changes in terms of the equilibria

$$\text{HIn} \quad \rightleftharpoons \quad \text{H}^{\cdot} + \text{In}'$$
(undissociated coloured)   (differently coloured anions)

and

$$\text{InOH} \quad \rightleftharpoons \quad \text{In}^{\cdot} + \text{OH}'$$
(undissociated coloured)   (differently coloured cations).
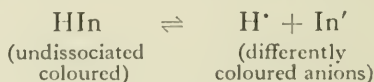
Such equilibria would be governed by the law of mass action throughout the neutralisation of the indicators, and therefore

$$\frac{[\text{H}^{\cdot}][\text{In}']}{[\text{HIn}]} = K_{\text{HIn}}$$

and

$$\frac{[\text{In}^{\cdot}][\text{OH}']}{[\text{InOH}]} = K_{\text{InOH}}$$

might be expected to give some quantitative measure of the colour changes undergone by the respective types of indicators. Hence the colour-change of a weak acid indicator at varying pH values may be expressed by

$$p\text{H} = p\text{K}_{\text{HIn}} + \log \frac{[\text{In}']}{[\text{HIn}]}$$

$$= p\text{K}_{\text{HIn}} + \log \frac{[\text{In}' \text{ colour}]}{[\text{HIn colour}]}$$

and of a weak base indicator by

$$p\text{OH} = p\text{K}_{\text{InOH}} + \log \frac{[\text{In}^{\cdot}]}{[\text{InOH}]}.$$

We have seen from the neutralisation curves of monobasic acids and of monoacid bases (Fig. 36), that though these reactions normally set up a change in hydrogen-ion concentration corresponding to 4 pH units, a variation of 1 pH unit occurs during the neutralisation from 1 to 10 per cent. and another change of 1 pH unit is introduced during the last phase, from 90 to 99 per cent. Hence, there occurs a change indicated by 2 pH units during neutralisation from 10 to 90 per cent., and moreover, it will be observed that this gradual change is almost a linear function of the degree of neutralisation. In the case of the weak acids or the weak bases which constitute the various indicators, it is found in general that the colour due to the other form is not discernible until 10 per cent. of the indicator has been converted into the salt form, and that the colour of the undissociated acid or base does not become completely masked to the eye until the indicator has undergone 90 per cent. neutralisation. Hence the pH range within which an indicator suffers a gradual change in colour is known as the *Transition Interval*, which, on theoretical grounds, should be given by the following expressions :—

(*a*) **Acidic Indicator : HIn.**

$$\text{Initial } p\text{H} = p\text{K}_{\text{HIn}} + \log \frac{10}{90}$$

$$= p\text{K}_{\text{HIn}} - 1 \text{ (approx.)}.$$

$$\text{Final } p\text{H} = p\text{H}_{\text{HIn}} + \log \frac{90}{10}$$

$$= p\text{K}_{\text{HIn}} + 1 \text{ (approx.)}.$$

∴ Transition interval = final pH — initial pH

$$= 2 \, p\text{H units (approx.)} = p\text{K}_{\text{HIn}} \mp 1.$$

(b) **Basic Indicator**: InOH.

Similarly   initial pOH $= p$K$_{\text{InOH}} -$ 1 (approx.)

and   final pOH $= p$K$_{\text{InOH}} +$ 1 (approx.).

∴ Transition interval $=$ final pOH $-$ initial pOH

$$= 2\ p\text{H units (approx.)}$$

$$= p\text{K}_{\text{InOH}} \mp 1.$$

Hence,   the initial pH $= p$K$_w - p$K$_{\text{InOH}} + 1$

and,   the final pH $= p$K$_w - p$K$_{\text{InOH}} - 1.$

We should therefore expect the colour change of an acidic indicator to begin at a pH value 1 unit below that of pK$_{\text{HIn}}$ and to end at a pH value 1 unit above, and that of a basic indicator to begin at a pH value 1 unit higher than pK$_w - p$K$_{\text{InOH}}$ and to finish at a value 1 unit below pK$_w - p$K$_{\text{InOH}}$.

Table 53, which gives a selected list of indicators suitable for use over the whole pH range from 0-14, shows that the transition interval for most indicators extends over about 2 pH units. The actual transition intervals are influenced by other factors such as (1) the sparing solubility of the indicator in one of its forms, (2) a difference in the intensity of the two coloured forms, (3) dichromatism of certain types of indicators, and (4) possible effects of the concentration of the indicator used.

The dissociation constants of a few indicators have been determined on the assumption that the colour changes are produced by the neutralisation of a monobasic acid. Two methods have been employed. One which is more suitable for one-coloured indicators, though it has been used for two-coloured indicators, involves the measurement of the proportion of indicator in a solution of known pH in the coloured form by means of a colorimeter or a spectrophotometer. The constant calculated from a series of such data by Rosenstein (*J. Amer. Chem. Soc.*, 1912, **34**, 1117 ; 1913, **35**, 1883) for phenolphthalein in solutions ranging from pH 8·96-9·95 reveals that the colour-change takes place in accord with the assumption that the intensity of the colour constitutes a measure of the extent of neutralisation of the indicator in producing red indicator-anions. Moreover, the amounts of neutralisation so found were in good agreement with those calculated from the concentrations of the reactants. The second method which is more appropriate for two-coloured indicators necessitates the measurement of the hydrogen-ion concentration of a solution of an indicator whose colour has been found to have been half-changed, *i.e.*, when the solution contains the

TABLE 53.

SELECTED INDICATORS.

pH Range.	Common Name.	Chemical Name.	Colour Change.	Used By:
0·0–1·3	Picric acid	Trinitrophenol	Colourless—yellow	M. and G.
0·0–2·0	Crystal violet	Hexamethyl-p-rosaniline	Green—blue	—
0·0–2·0	Malachite green	Tetramethyl di-p-aminotriphenyl-carbinol	Yellow—green	S.
0·1–3·2	Methyl violet	Mixture	Yellow—violet	C.
0·5–2·5	Metacresol purple	m-Cresol sulphone phthalein	Red—yellow (also pH 7·6–9·2 yellow—purple)	
1·2–2·3	Metanil yellow	m-Sulphobenzene-azo-di-phenylamine	Red—yellow	S.
1·2–2·8	Xylenol blue	p-Xylenol sulphone phthalein	Red—yellow (also pH 8·0–9·6 yellow—blue)	C. and L.
1·2–2·8	Thymol blue	Thymol sulphone phthalein	Red—yellow (also pH 8·0–9·6 yellow—blue)	C. and L.
1·3–3·2	Tropæolin OO	Phenylaminoazobenzene-sulphonic acid	Pink—yellow	S.
1·5–5·0	Benzopurpurin	Ditolyldisazobi-β-naphthylamine-β-sulphonic acid	Blue—violet—orange	S.
1·7–4·4	β-Dinitrophenol	2 : 6 Dinitrophenol	Colourless—yellow	M. and G.
2·0–4·7	α-Dinitrophenol	2 : 4 Dinitrophenol	Colourless—yellow	M. and G.
2·9–4·0	Methyl yellow	Dimethylanilinoazobenzene	Red—yellow	S.
3·0–4·6	Bromophenol blue	Tetrabromophenol-sulphonephthalein	Yellow—blue	C. and L.
3·0–5·0	Congo red	Diphenyldisazobinaphthionic acid	Blue—red	—
3·1–4·4	Methyl orange	p-Benzenesulphonic acid-azo-dimethyl-aniline	Red—yellow	S.
3·2–4·8	Bromochlorophenol blue	Dibromodichlorophenol-sulphonephthalein	Yellow—blue	C.
3·5–4·5	Ethyl orange	p-Benzenesulphonic acid-azo-diethylaniline	Pink—yellow	—

TABLE 53 (*continued*).

pH Range.	Common Name.	Chemical Name.	Colour Change.	Used By :
3·5–5·7	—	p-Benzenesulphonic acid-azo-α-naphthyl-amine	Red—orange	S.
3·7–5·2	Sodium alizarine sulphonate	Sodium alizarine sulphonate	Yellow—violet (also pH 10·0–12·0 red—yellow)	
3·9–5·9	ε-Dinitrophenol	2 : 3 Dinitrophenol	Colourless—yellow	—
4·0–5·6	Bromocresol green	Tetrabromo-m-cresol sulphonephthalein	Yellow—blue	—
4·0–6·0	γ-Dinitrophenol	2 : 5 Dinitrophenol	Colourless—yellow	C.
4·0–7·0	Chrysoïdin	Benzene-azo-m-phenylenediamine	Orange—yellow	M. and G.
4·2–6·3	Methyl red	o-Carboxybenzene-azo-dimethylaniline	Red—yellow	—
4·3–6·3	δ-Dinitrophenol	3 : 4 Dinitrophenol	Colourless—yellow	S. : C. & L.
4·4–6·2	Ethyl red	o-Carboxybenzene-azo-diethylaniline	Red—yellow	—
4·4–6·6	Lacmoid	—	Red—blue	—
4·6–6·6	Propyl red	o-Carboxybenzene-azo-di-n-propyl-aniline	Red—yellow	S.
4·8–6·2	Cochineal	—	Yellow—lilac	—
5·0–7·0	Chlorophenol red	Dichlorophenol sulphonephthalein	Yellow—red	—
5·0–7·0	p-Nitrophenol	p-Nitrophenol	Colourless—yellow	C.
5·0–8·0	Litmus, Azolitmin	—	Red—blue	S.
5·2–6·8	Bromocresol purple	Dibromo-o-cresol sulphonephthalein	Yellow—purple	S.
5·4–7·0	Bromophenol red	Dibromophenol sulphonephthalein	Yellow—red	C. and L.
6·0–7·6	Bromothymol blue	Dibromothymol sulphonephthalein	Yellow—blue	C.
6·5–8·5	m-Nitrophenol	m-Nitrophenol	Colourless—yellow	M. and G.
6·8–8·0	Aurine	p-Rosolic acid	Brown—red	S.
6·8–8·0	Neutral red	Dimethyldiaminotoluphenazine	Red—yellow	S.
6·8–8·4	Phenol red	Phenolsulphonephthalein	Yellow—red	C. and L.
7·0–8·0	Quinoline blue	Cyanine	Colourless—violet	—
7·2–8·8	Cresol red	o-Cresol sulphonephthalein	Yellow—red	C. and L.
7·3–8·7	—	α-Naphtholphthalein	Red—blue	—
7·6–8·9	Tropæolin OOO	p-Sulphobenzene-azo-α-naphthol	Brownish-yellow—red	S.

TABLE 53 (*continued*).

pH Range.	Common Name.	Chemical Name.	Colour Change.	Used By:
7·8–9·2	Turmeric	—	Yellow—orange	—
8·0–9·6	Xylenol blue	p-Xylenol sulphonephthalein	Yellow—blue (also pH 1·2–2·8 red—yellow)	C. and L.
8·0–9·6	Thymol blue	Thymol sulphonephthalein	Yellow—blue (also pH 1·2–2·8 red—yellow)	C. and L.
8·2–9·8	Cresolphthalein	o-Cresolphthalein	Colourless—red	C. and L.
8·3–10·5	Phenolphthalein	Phenolphthalein	Colourless—red	S.: C. & L.
9·3–10·5	Thymolphthalein	Thymolphthalein	Colourless—blue	S.
10·0–12·0	Alizarine yellow GG (Salicyl yellow)	p-Nitrobenzene-azo-salicylic acid	Colourless—yellow	M. and G.
10·0–12·0	Sodium alizarine sulphonate	Sodium alizarine sulphonate	Brownish-red—yellow	S.
10·5–11·5	Azo blue	Ditolyldisazobi-α-naphthol-4-sulphonic acid	Violet—pink	—
10·8–12·8	Nitramine	Picrylmethylnitramine	Colourless—orange brown	S.
11·0–13·0	Tropæolin O	p-Sulphobenzene-azo-resorcin Benzene-azo-β-naphthol	Yellow—orange brown	S.
11·5–14·0	Orange G.	γ-Disulphonic acid	Yellow—pink	—

indicator in equal concentrations in its acid form and in its alkaline form. The half-way colour may be ascertained by having two tubes of the same size and shape such that one contains a certain amount of the indicator completely in the acid form and the other the same amount of indicator but completely changed into the alkaline condition. If one tube is then placed on the top of the other and illuminated at the bottom, the tint on looking down through the two tubes will correspond to the half-way tint for the particular concentration of indicator used. If now, a tube of double length and the same cross-section is taken and filled with a solution containing twice the amount of indicator inserted in the separate solutions and whose colour has been adjusted by the addition of buffer agents such that the tint, when the liquid has been similarly illuminated, is identical with the half-way colour, it is only necessary to determine the hydrogen-ion concentration of the solution. Then if this half-way colour change is produced at the half-neutralisation of the indicator, considered either as a mono-valent acid (or base) it follows that $pH = pK_{HIn}$ (or $pOH = pK_{InOH}$).

A selection of indicator constants is given in Table 54, together

TABLE 54.

DEPENDENCE OF TRANSITION INTERVAL ON DISSOCIATION CONSTANT OF INDICATOR.

Indicator.	pK.	Transition Interval, pH.	
		Theoretical.	Practical.
Thymol blue (acid range) .	1·7	0·7–2·7	1·8–2·8
Thymol blue (alk. range) .	8·9	7·9–9·9	8·0–9·6
Methyl orange .	3·7	2·7–4·7	3·0–4·6
Bromophenol blue .	4·1	3·1–5·1	3·1–4·4
Methyl red .	5·1	4·1–6·1	4·2–6·3
Ethyl red .	5·4	4·4–6·4	4·4–6·2
Propyl red .	5·4	4·4–6·4	4·6–6·6
Bromocresol purple .	6·3	5·3–7·3	5·2–6·8
Bromothymol blue .	7·1	6·1–8·1	6·0–7·6
Cresol red .	8·1	7·1–9·1	7·2–8·8
Phenol red .	7·8	6·8–8·8	6·8–8·4
α-Naphtholphthalein	8·4	7·4–9·4	7·3–8·7
Thymolphthalein .	9·2	8·2–10·2	9·3–10·5
Phenolphthalein .	9·7	8·7–10·7	8·3–10·5

with the predicted useful ranges of these indicators and the ranges for which they have been found to be available. The colour changes of azo-indicators such as methyl orange and methyl red are really due to the indicators behaving as bases (see p. 204), but

in the values given they are treated as if they were acids. The sulphone phthalein indicators of Clark and Lubs are dibasic, but as suggested by Clark the colour changes are functions of the weak stages of ionisation, namely, the neutralisation of the phenolic groups, and not to the comparatively strong sulphonic acid group ionisations. Kolthoff has, moreover, shown that their behaviour may be satisfactorily considered in terms of the simple linear equation given above.

The Ostwald theory of the colour changes of indicators, being due to ionisation, is inadequate. It does not, for instance, explain why the solid salt of phenolphthalein is red. It is hardly fitting in a book of this type to enter into a lengthy discussion of the elaborate theories of colour and constitution of organic compounds. There is no doubt that many colour changes can be attributed to changes in constitution. Thus if ionisation were the sole cause of the change in colour, it is difficult to understand why certain indicators, e.g., tropæolin OOO, and hæmatein, should not undergo their transitions instantaneously instead of requiring time. It may be that the conception of Wolfgang Ostwald, that the colour change of an indicator is traceable to colloidality in the solution and therefore that the colour assumed by a solution would be connected with the size of the dispersed particles, provides an explanation for such time reactions. The mechanism of the change brought about by hydrogen- and hydroxyl-ions might therefore be due to reactions with a colloidal electrolyte with the consequent changes in the magnitude of the micellar ions. Baly accounts for the colour of solutions on a purely physical theory based upon his extensive observations of absorption spectra. Such a theory gains support when it is remembered that colour is essentially an optical property and that as light is electromagnetic in nature, absorption involves a change in energy dependent upon the dissolved molecules.

Nevertheless, the theory that colour change is one of tautomeric change affords plausible explanations of the ultimate substances which are formed possessing colour, in that they contain chromophoric quinone groups. As Kolthoff states, however (*Indicators*, p. 239) the chromophoric theory gives " no explanation of the change, but calls attention to a phenomenon that accompanies the colour change. The colour change is accompanied by a change in constitution, but this is not the cause of the colour change." Simply, because the two changes take place simultaneously, it is not logical to conclude that a change in constitution is the cause of a change in colour, any more than it is to suggest that a change in colour is the cause of the change in constitution. In the case

of phenolphthalein, the researches of Friedländer, Bernsthen, Hantzsch and pupils, show that the colourless compound contains a lactone ring whereas the red salt formed by the interaction of alkalis has the chromophoric quinoid group, thus :

C_6H_4OH C_6H_4OH C_6H_4ONa

$+ 2NaOH \rightarrow$

$+ 2H_2O$

Lactone ring   Quinone group
(colourless).   (red).
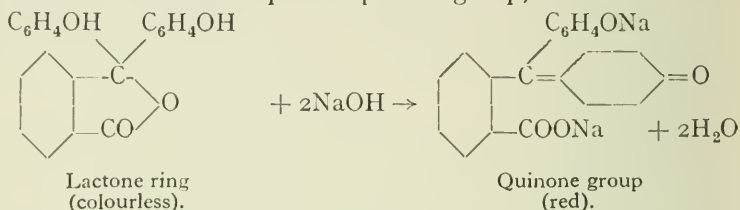
The colour of an indicator solution may be determined by the equilibrium existing between tautomers. Thus the normal form of p-nitro-phenol is a true nitro-body which exists in solution in tautomeric equilibrium with nitrolic acid. Whereas the former form is colourless, the latter is yellow. The equilibrium may be represented

Colourless.   Yellow.
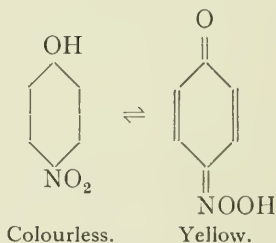
The colours of the sulphonephthaleins have been attributed by Lubs and Acree to the opening of a lactoid ring and the resulting formation of a quinoid group, to be followed by the ionisation of the sulphonic acid and phenolic groups through neutralisation with a strong base. As an example, we shall consider the stages in the production of colour by phenol sulphonephthalein, $i.e.$, phenol red. In acid solutions it is supposed to be present in an equilibrium between its two tautomers,

Colourless   Pale yellow
(lactoid ring)   (quinoid group)
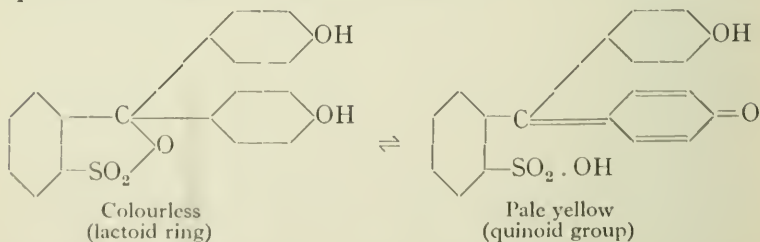
though owing to the strongly acidic nature of the sulphonic acid group it is believed that the quinoidal body must predominate.

On the addition of an alkali, the sulphonic acid group will be the first to be reacted upon and the ionisation of the salt thus formed is considered to have very little effect upon the colour. When, however, more alkali is added the phenolic group enters into re-action and it is the ionisation thus brought about which, it is believed is responsible for the transformation from the yellow to the characteristic deep red colour of the indicator. These two stages are therefore

Pale yellow.

Pale yellow.

Deep red.
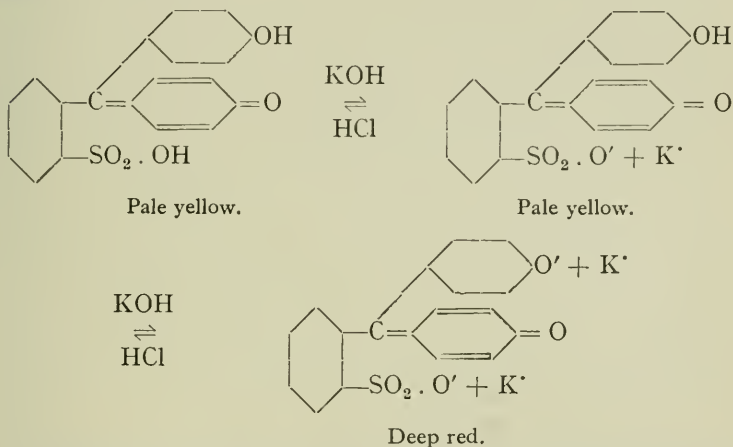
We shall now direct our attention to the explanation afforded by the chromophoric theory of the behaviour of indicators con-taining the azo-group, e.g., methyl orange and methyl red. In alkaline solution they possess the azo linkage, but on making the solution acid a benzene group undergoes transformation of the quinoid type. Methyl yellow, dimethylaminoazobenzene, is the simplest type of an azo indicator. Its yellow form, which is present in alkaline solution, is a very feeble base, and then contains the azo grouping, but on rendering the solution acidic it assumes the property of being a strong base, due to an intramolecular change in forming a quinoid group, and at the same time the solution becomes red. This transformation may be represented thus :

Azo linkage : yellow : in alk. solution.

Quinoid group : red : in acid solution.

or ionically, as

$$\langle\ \rangle\!-\!N\!=\!N\!-\!\langle\ \rangle N(CH_3)_2 + H^{\boldsymbol{\cdot}}$$

$$\rightleftharpoons \langle\ \rangle NH\!-\!N\!=\!\langle\ \rangle\!=\!N(CH_3)_2{}^{\boldsymbol{\cdot}}.$$
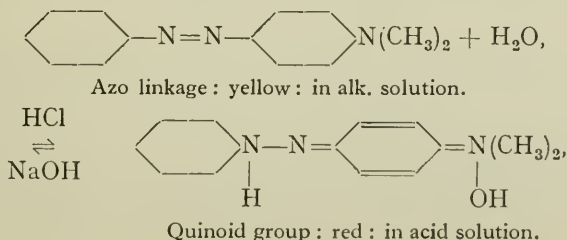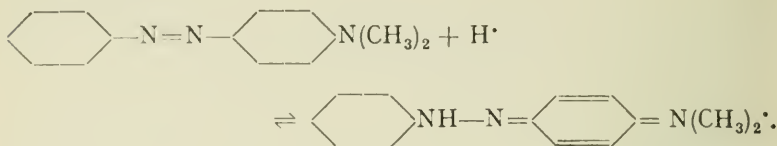
The behaviour of dimethylaminoazobenzene towards an acid is thus seen to be that of a base. On the other hand, the hydrogen-ion concentration of a solution giving a half-way tint corresponds to pH $3\cdot2$, and therefore, if it were an acid, its dissociation constant would be $10^{-3\cdot2}$, corresponding to that of a fairly strong acid. Actually, this is the hydrolysis constant of its salt with a strong acid with alkali, and therefore its basic constant $= K_w/10^{-3\cdot2} = 10^{-11}$.

The various colours of the indicators of this class, such as those of methyl orange and methyl red, can be accounted for by similar changes in structure, but the actual processes of colour change can only be placed on a quantitative footing in terms of electrolytic dissociation, as we have just seen to be the case with dimethylamino-azobenzene. This will be seen more forcibly from a study of the colour change of methyl orange. In its solid form, it is the sodium salt of dimethylaminoazobenzene-sulphonic acid which on dissolution in water imparts to it a yellow colour, due, we may reasonably imagine, to the organic anion, whilst on the addition of acid the red form is developed. Salm (*Z. physikal. Chem.*, 1907, **57**, 471) found that the pH of the solution at $18°$ C. to give half-way colour was $3\cdot3$, and therefore if we regard the transition from the red form to the yellow form by means of an alkali, methyl orange would appear to be a fairly strong monobasic acid whose constant is $10^{-3\cdot3}$. It is of interest that Tizard's results (*J. Chem. Soc.*, 1910, **97**, 2477) obtained by the first method described on page 208, led to an apparent acidic constant of $10^{-3\cdot4}$ at $25°$ C. As before, this constant is merely the hydrolysis constant of the weak indicator base — strong acid salt. It is likely that the change is most satisfactorily represented on the basis of the " Zwitter " ion theory, whence the yellow anion is

$$(CH_3)_2N . R . SO_2O'$$
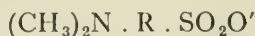
in which R is $C_6H_4 . N = N . C_6H_4$, and the red form, the " Zwitter " ion

$$\boldsymbol{\cdot}H(CH_3)_2N . R . SO_2O'$$
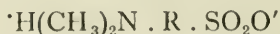
and therefore the change in colour is given by

$$\boldsymbol{\cdot}H(CH_3)_2N . R . SO_2O' + OH' \rightleftharpoons (CH_3)_2N . R . SO_2O' + H_2O$$
$$\text{Red.} \qquad\qquad\qquad\qquad\qquad\qquad \text{Yellow.}$$
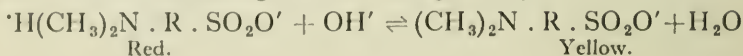
Using the symbols adopted on page 176, we find that

$$\frac{[Z][OH']}{[A']} = k_b = \frac{[Red][OH']}{[yellow]}.$$

Hence at 18°,
$$pk_b = p\mathrm{K}_w - p\mathrm{K}_a$$
$$= 14 \cdot 1 - 3 \cdot 3$$
$$= 10 \cdot 8.$$

A more recent value was obtained at 18° by Kolthoff (*Rec. trav. chim.*, 1925, **44**, 68) of $pk_b = 10 \cdot 7$ and Thiel and Dassler (*Ber.*, 1923, **56**, 1667) of $10 \cdot 5$ at 25° C. Whereas these considerations give no reasons why the ampholytic or " Zwitter " ion should be different in colour from the anion, a possible clue is to be found in the tautomeric rearrangements within the ions, thus :

Red form.

Yellow form.
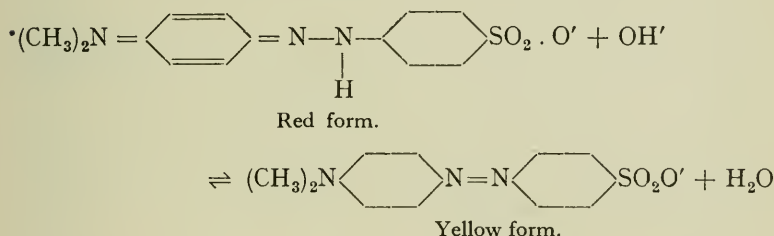
The acidic dissociation, *i.e.*, the reaction of the ampholytic ion with hydrogen-ions forming cations containing the free sulphonic acid, are without effect upon the colour of the solution. This is also true for methyl red, which is
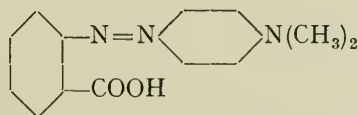
and in solution forms the " Zwitter " ion
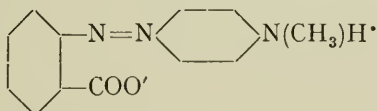
The acid dissociation has the constant, $k_a = 2 \cdot 5 \times 10^{-3}$ or $pk_a = 2 \cdot 60$. The pH at half-neutralisation is therefore $p\mathrm{K}_w - pk_a = 11 \cdot 5$. This mode of ionisation, however, is unimportant as it has no effect on the colour change, for as in the previous two examples, this is connected entirely with the basic neutralisation. Again the " Zwitter " ion is red and the anion yellow, and the value

of $pk_b = 9 \cdot 15$ and therefore the pH at half-way colour change is $14 \cdot 14 - 9 \cdot 15 = 5 \cdot 0$ at $18°$ C.

It will be concluded from the foregoing discussion that, whatever may be the true cause of the colour changes of indicators, the application of the ionisation theory and the law of mass action have led to a remarkably useful working hypothesis. This will be appreciated in connexion with the methods to be described for the approximate measurement of hydrogen-ion concentrations without the aid of standard buffer solutions, as in the methods of Michaelis, Gillespie, and McCrae.

Approximate Colorimetric Methods of Determining pH.

Two types of methods of finding the approximate pH value of a solution are available.

One type is based on theoretical principle that the ionisation of an indicator acid considered as a monobasic acid constitutes a measure of the degrees of change undergone in the colour. Hence if the extent of neutralisation is known and the resulting colour observed, it is possible to calculate from a knowledge of the apparent dissociation constant of the indicator the hydrogen-ion concentration which produces any particular shade of colour. Thus, we have seen that

$$pH = pK + \log \frac{[In']}{[HIn]}$$

and if x be the percentage of neutralisation of HIn, then

$$pH = pK + \log \frac{x}{100 - x}.$$

The second type involves the matching of the colour obtained when a definite quantity of indicator is added to a definite volume of liquid undergoing test, with that of one of a series of standard buffer solutions differing by about $0 \cdot 2$ pH unit (being of the same volume), and each containing the same amount of indicator solution. These colours must be matched by viewing through the same thickness or depth of solution. Of the two kinds of methods it is probable that the results obtained by the latter will be the more accurate. The difficulties attendant on colorimetric methods are such that the limit of accuracy attainable probably does not extend much beyond $0 \cdot 1$ pH unit.

In all these methods the validity of Beer's law is assumed ; namely, that when light transmitted through two solutions, of different depth or thickness and having different concentrations

of the solute which produces the particular colour and causes the two solutions to appear identical, then provided the conditions of illumination are the same, the product of the concentration of one solution and the distance through which the light passed, is equal to the product of the concentration of the other solution and the distance travelled through it by the light. Hence if c_1 and d_1 be the respective concentration and depth of one solution, and c_2 and d_2 of another, then

$$c_1 \times d_1 = c_2 \times d_2.$$

In colorimetric work, it is usual to keep the distances through which the light passes in the various solutions the same, *i.e.*, $d_1 = d_2$, and therefore it is essential the indicator concentrations of liquids in the comparison tubes shall be the same. In the case of two coloured indicators a difficulty arises on account of the possible differences in the transmission coefficients of the various light radiations which pass through a solution. For this reason, it is a matter of some importance to employ suitable illumination. Clark points out that all the sulphone phthalein indicators may be used in electric light. Bromothymol blue and thymol blue require light which is strong in blue radiations. It is in this regard that the absorption spectra of indicator solutions may be of assistance, of which descriptions for certain indicators will be found in Prideaux' useful book, *The Theory and Use of Indicators*, London, 1917.

Colorimetric Methods without Standard Buffer Solutions.

These methods are based on the assumption that the colour changes of the various indicators employed are quantitatively proportional to the amounts of the neutralisation undergone by the indicator if considered as monobasic acids. Consequently, if the apparent dissociation constant of the indicator be known and some satisfactory means can be devised to measure the colour changes, then the pH of a solution giving any particular colour can be readily calculated. Thus we have seen that when x is the actual amount of neutralisation,

$$p\text{H} = p\text{K}_{\text{HIn}} + \log \frac{x}{1 - x}$$
$$= p\text{K}_{\text{HIn}} + \log \frac{\text{colour of alkaline form}}{\text{colour of acid form}}.$$

In the case of one-colour indicators, colourless when in the acid form and coloured in the alkaline form, the extent to which

the indicator has been reacted upon will be given by the depth
of colour. Thus, if a definite amount of such an indicator in a
solution produced a depth, or intensity of colour, equal to a frac-
tion, C, of that which would have been produced had that concen-
tration of indicator been converted entirely into the alkaline form,
then

$$pH = pK_{HIn} + \log \frac{C}{1 - C}.$$

Methods based on these principles are the following :—

(1) *Wedge methods of Bjerrum and McCrae.*
(2) *Colorimeter method of Gillespie.*
(3) *" Drop Ratio " Comparator method of Gillespie, and*
(4) *Colour Intensity method of Michaelis.*

These individual methods will now be discussed.

Wedge Methods.

This method appears to have first been adopted by Bjerrum
(*Die Theorie der alkalimetrischen und azidimetrischen Titrierungen*,
Stuttgart, 1914, also in Ahren's *Sammlung*, Vol. 21) for the deter-
mination of indicator constants of two-colour indicators. He
used a rectangular box having glass sides. It was about 30 cm.
in length, 10 cm. high and 2 cm. thick, and was divided into two
wedge-shaped compartments by a piece of glass inserted diagonally.
One compartment was filled with a solution containing the in-
dicator completely transformed into the acid form, and the other
with the same amount of indicator completely converted into the
alkaline form. A narrow cell of 2 cm. wide and having narrow
glass apertures in the two opposite ends moved along on the
top of this vessel. In it was placed a buffer solution of known
*p*H and having the same concentration of indicator as the solutions
used in the lower vessels. The cell was moved until a position
was found that the colour of the solution in the upper cell was the
same as that produced by light passing through the two slices of
the wedge immediately below. This was made possible by a
slit arrangement attached to the small test-cell. Then, by measur-
ing the width of the two solutions respectively coloured by the
acid- and alkaline-forms of the indicator, it was known what
proportion of the indicator in the test-cell had been converted
into the alkaline form. It was possible, moreover, to adjust the
*p*H of the test solution until the indicator colour agreed with that
shown when light passed through equal widths of the two liquids

in wedges, and so obtain the value of $p\mathrm{K}_{\mathrm{HIn}}$. The principle of this method will be understood from Fig. 51, which is a plan of a two-wedge cell arrangement. On looking through a section of liquid in the wedge cells, the observed colour will be composed of the light transmitted through a portion of solution tinted by the alkaline form of the indicator and a portion coloured by the acid form of the indicator. Thus, in the figure the colour in the test-cell is represented as matching the colour produced by the thickness of liquid, 60 per cent. of which corresponds to the acid form of the indicator and 40 per cent. to the alkaline form. Hence the colour produced by the same concentration of indicator in the unknown solution shows that the indicator has suffered 40 per cent. neutralisation and therefore, if
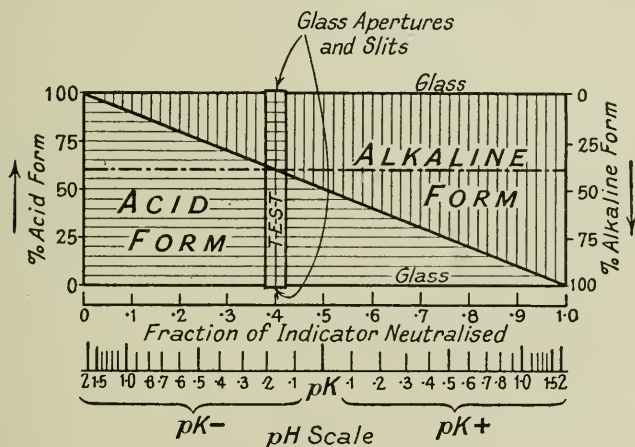
FIG. 51.—Principle of Colorimetric Determinations of pH Values.

$\mathrm{K}_{\mathrm{HIn}}$ be known, the pH can be readily calculated as described on page 206. Scales may be affixed to such a colorimeter showing (a) the fraction of neutralisation of the indicator represented by each different shade of colour when viewed through the slits on the opposite sides of the apparatus, and (b) the pH value referring to the various colours in terms of $p\mathrm{K}_{\mathrm{HIn}}$. Such scales are shown in Fig. 51. The pH scale shows clearly that determinations are more likely to be accurate round about half-neutralisation, for a difference of 0·1 pH unit corresponds to a much greater variation in neutralisation than when $p\mathrm{H} = p\mathrm{K}_{\mathrm{HIn}} \pm$ 1·0. Whenever possible indicators should be chosen in order that the pH of the solution under test should lie within $p\mathrm{K}_{\mathrm{HIn}} \mp$ 0·7. In Table 55 are given the actual amounts of neutralisa-

tion corresponding to changes of 0·1 pH unit of those indicators which can be treated as weak monobasic acids. The values are indicated for half neutralisation, $i.e.$, when pH $= pK_{HIn}$ of certain indicators which may be employed in this method ($cf.$ Table 54).

TABLE 55.

RELATIONSHIP BETWEEN NEUTRALISATION OF AN INDICATOR, GILLESPIE'S " DROP RATIO " AND pH.

Per cent. neutralised	9·1	11·2	13·7	16·6	20·0
pH $= pK$ −	1·0	0·9	0·8	0·7	0·6
" Drop Ratio "	$\frac{1}{9}$	—	$\frac{1\frac{1}{2}}{8\frac{1}{2}}$	—	$\frac{2}{8}$
Per cent. neutralised	24·0	28·5	33·4	38·7	44·3
pH $= pK$ −	0·5	0·4	0·3	0·2	0·1
" Drop Ratio "	—	$\frac{3}{7}$	—	$\frac{4}{6}$	—

Half neutralised	50	Bromophenol blue	Methyl red	Bromocresol purple	Bromothymol blue	Phenol red	Cresol red	Thymol blue
pH $=$	$pK_{HIn}=$	4·1	5·0	6·3	7·1	7·7	8·1	8·8
" Drop Ratio "	$\frac{5}{5}$	—	—	—	—	—	—	—

Per cent. neutralised	55·8	61·3	66·7	71·6	76·0
pH $= pK$ +	0·1	0·2	0·3	0·4	0·5
" Drop Ratio "	—	$\frac{6}{4}$	—	$\frac{7}{3}$	—
Per cent. neutralised	80·0	83·4	86·3	88·8	90·9
pH $= pK$ +	0·6	0·7	0·8	0·9	1·0
" Drop Ratio "	$\frac{8}{2}$	—	$\frac{8\frac{1}{2}}{1\frac{1}{2}}$	—	$\frac{9}{1}$

A modified form of this apparatus has been introduced by McCrae ($The\ Analyst$, 1926, **51**, 287). It is shown in Fig. 52. The two triangular glass cells which are placed together to form a divided rectangular cell are covered with metal provided with lateral slots. The triangular cells have an internal dimension of 15 cm. along the long side forming the right angle, and 3·5 cm. along the other side, the hypotenuse thus being about 15·4 cm. The depth of the cell is 4·7 cm. and the capacity at 125 c.c. A sliding holder, carrying a rectangular glass cell, internal dimensions 3·5 cm. × 1·4 cm. × 4·7 cm., moves along the top of the combined cells. The capacity is about 2·4 c.c. There are nine slots, 4 cm. high and 1·2 cm. wide which are separated from one another by 0·4 cm. Looking through the middle slot a colour is seen which is that of the half-way change of the indicator, and therefore pK_{HIn} $= p$H. The colours seen through the slots on each side refer to pH values which increase or decrease by amounts of 0·2 pH unit,

with the exception of the two end slots that correspond to differences of 0·4 *p*H. The reason for this will be apparent from either the scales on Fig. 51 or Table 55. To ascertain the *p*H value of a solution using McCrae's apparatus, about 300 c.c. of the solution are treated with sufficient of the appropriate indicator to impart a good strong colour, which is then poured into each of the two triangular cells and also into the small rectangular cell. The full acid colour is developed in one of the triangular cells by the addition of a few drops of hydrochloric acid, and the full alkaline colour in the other by means of a little sodium hydroxide. Uniformity of these colours is ensured by stirring, after which the
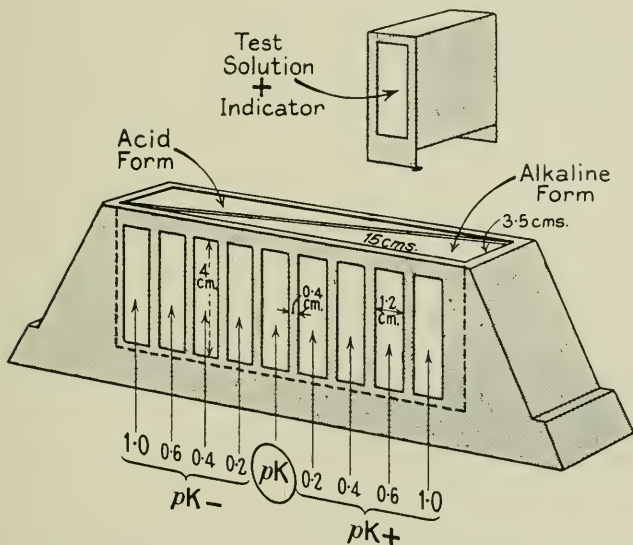
Fig. 52.—McCrae's Modification of the Wedge Colorimeter.

cover is placed over the triangular cells and the metal carrier with the small rectangular cell placed on top. This is moved along until the tint of the solution, as viewed against a white background, matches the colour through a slot immediately below. If the solution available is insufficient for the above procedure, then distilled water may be substituted in the cells and coloured with the amount of indicator to give the same concentrations in the solution undergoing examination and in the solutions in the lower vessels. Thus if 250 c.c. of water used in the triangular cells required 1 c.c. of indicator solution, and 25 c.c. of unknown solution were available then this volume would require $\frac{1}{10}$ c.c. of indicator solution.

Gillespie's Colorimetric Methods.

(1) Colorimeter Method.

The colorimeter devised by Gillespie (*J. Bact.*, 1921, **6,** 399) is shown in Fig. 53. The tubes A and B are fixed such that their bottoms are on a level with one another. The outer vessels, which are identical, are also fixed at the same level and are equally illuminated from the bottom. The inner vessel in vessel I is movable upwards and downwards, and has a pointer which travels along
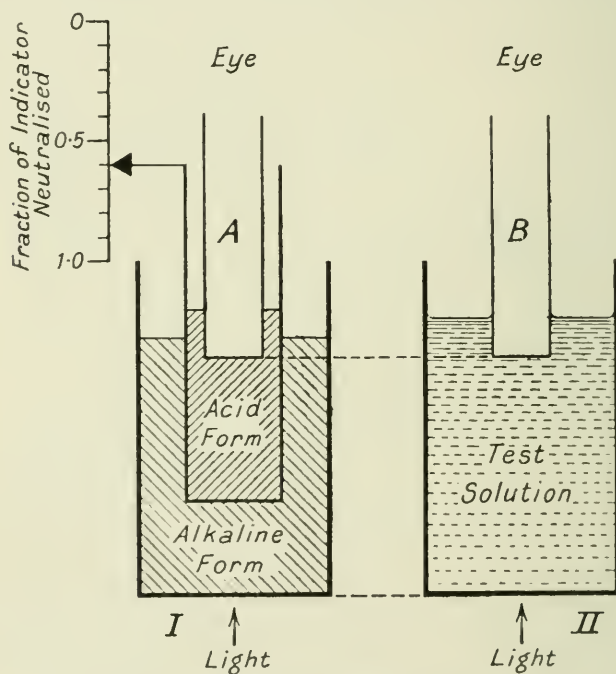
FIG. 53.—Diagram of Gillespie's Colorimeter.

a scale showing the percentage amount of indicator neutralised to give a particular colour. If the solution to be tested is both clear and colourless no solutions are placed in A and B. The test solution, with a suitable quantity of a suitable indicator, is placed in vessel II, such that the end of tube B is immersed. Water, having the same indicator concentration, is poured into the two compartments of vessel I, and that in the inner vessel rendered sufficiently acidic to generate the full acid colour, whilst that in the outer vessel is treated with alkali to produce the full

alkaline colour. By observing the two colours produced in I and II from above, the vessels being suitably enclosed, it is possible to find a position of the movable cell at which the resulting colours will appear the same. Then by measuring the lengths of the columns of the acid and alkaline liquids, the amount of neutralisation undergone by the indicator in the test-cell II is known, whence the pH can be calculated. In the diagram, the pointer represents 60 per cent. of indicator in the acid form and 40 per cent. in alkaline form.

Should the solutions be either turbid or coloured, then the tube A is filled with the test solution without the indicator to a height equal to that between the bottom of the tube and the base of the apparatus, whereas the same quantity of distilled water is inserted in B. The determination is then carried out as above described. In this way, compensation for colour or turbidity is obtained.

(2) " Drop-Ratio " Method.

This method which Gillespie (*J. Amer. Chem. Soc.*, 1920, **42,** 742) proposed is especially useful for rapid approximate determinations. The colours corresponding to different pH stages in the colour change of an indicator are obtained by having a series of two identical glass test-tubes, one placed immediately behind the other and containing the same volume of water. They may be conveniently inserted in a test-tube rack. To each pair of tubes 10 drops of an indicator solution of suitable concentration are added, so that if one tube receives one drop then the other must receive nine drops. The acid colour is developed in one tube by the addition of a suitable acid or acid salt, and the alkaline form in the other. The colour observed when viewed directly through the two tubes will be the result of so much in the alkaline form and so much in the acid form. Hence, a solution matching such a colour, provided that 10 drops of indicator solution had been added to it, would have a pH value given by

$$pH = pK_{HIn} + \log \frac{\text{drops of alkaline form}}{\text{drops of acid form}}.$$

Gillespie calls the ratio in the last term, the " drop ratio " and

therefore $pH = pK_{HIn} + \log$ " drop ratio."

The " drop ratios " which correspond to the different amounts of neutralisation are given in Table 55. This method of measuring

the volume of a solution is far from satisfactory for accurate comparisons. The table shows the variations of 0·2 pH for the different drop ratios from that of pK$_{HIn}$. Moreover, the rough nature of the method was allowed for by Gillespie, for when an acid indicator is neutralised to the extent of 13·7 per cent., the ratio $\frac{\text{alkaline form}}{\text{acid form}} = \frac{13\cdot7}{86\cdot3}$, whereas the nearest drop ratio is $\frac{1\frac{1}{2}}{8\frac{1}{2}}$. Similarly the drop ratio for 28·5 per cent. is $\frac{3}{7}$, and for 38·7 per cent. $\frac{4}{6}$. It would also be more satisfactory to employ a microburette to measure out the indicator, and in comparing the colour of the unknown solution to view it through a tube of the same diameter filled with water, so that any error introduced by the different thicknesses of liquid may be eliminated. Rectangular glass cells of equal size, instead of the test-tubes, would probably facilitate colour matching in that each pair of cells could be placed close together. The tubes used by Gillespie were 15 cm. long and 1·5 cm. in diameter, and the solutions were about 5 to 6 c.c. in volume.

Gillespie found that the following indicators could be employed : bromophenol blue, methyl red, bromocresol purple, bromothymol blue, phenol red, cresol red and thymol blue. His values of pK$_{HIn}$ are given in Table 55. With the exception of the solutions of bromocresol purple and phenol red whose concentrations should be 0·012 per cent. and 0·004 per cent. respectively Gillespie recommends that the concentration of the indicator solution should be 0·008 per cent. The acid colour should be developed by adding 1 c.c. of N/20 solution of NaOH to 10 c.c. of solution when using bromophenol blue, and 1 drop only when using either methyl red, bromocresol purple, bromothymol blue or phenol red, but in the case of cresol red and thymol blue 1 drop of a 2 per cent. solution of KH$_2$PO$_4$ should be added in order to prevent the appearance of the further colours arising from the acid ranges of these two indicators. Hatfield (*J. Amer. Chem. Soc.*, 1923, **45,** 930) advocates, on the grounds of the enhanced stability of indicator colours, extending over a period of from 1 to 2 months, the use of weak acids or bases for the development of the acid or alkaline colours. Thus he uses a N-acetic acid solution with bromophenol blue and methyl red, and a 7 gram KH$_2$PO$_4$ per litre solution with cresol purple, bromothymol blue, phenol red, cresol red and thymol blue to the solutions to produce the respective acid colours. The alkaline colours of bromophenol blue, methyl red, bromocresol purple and bromothymol blue are obtained in a solution

containing 18 grams $Na_2HPO_4,12H_2O$ per litre, and those of bromocresol purple, bromothymol blue, phenol red, cresol red and thymol blue with a 1 gram Na_2CO_3 per litre solution.

If it is desired to make pH measurements by either of the two methods of Gillespie with a one-coloured indicator, say colourless in the acid condition, then the vessels in which the indicator is put and transformed to give the acid colour, may either be elimi-nated altogether or merely filled with distilled water. The latter procedure applies more particularly to the colorimeter method, for it is scarcely necessary in the tube method.

Michaelis' Method with One-Coloured Indicators.

Many one-coloured indicators behave as if they were weak monobasic acids whose anions alone are coloured. Owing to their weakness, the ionisation of the free indicator acids is so slight that the indicators in acid solutions are colourless. On reaction with an alkali the formation of a strongly ionised salt, NaIn. leads to the production of colour. Michaelis and Gyemant (*Biochem. Zeitsch.*, 1920, **109,** 165) have shown that the intensity of this colour compared with that obtained when the indicator is fully transformed into the indicator salt, NaIn, *i.e.*, in alkaline solutions, constitutes a measure of the degree of neutralisation, so that if the pK$_{HIn}$ be known, the pH value can easily be calculated. In-stead, however, of making comparisons of different intensities of colour, they adopt a somewhat indirect method by which the same relations are obtained. Thus they add to a measured amount of solution (5 to 10 c.c.), whose pH value is to be found, sufficient indi-cator solution, the volume of which is accurately measured (0·2 c.c. to 1·0 c.c.), to impart to the solution a pale but definite coloration. This colour is now produced by adding to a quantity of N/100— NaOH solution just that quantity of indicator to give it when the resulting solution is made up to the volume of the test solution. It is necessary that the volume of indicator should be accurately known, and it should therefore be measured out from a burette, reading to 0·01 c.c. The accuracy can be somewhat increased by using for the latter purpose an indicator solution, diluted 10 or 20 times. Thus, if T c.c. of indicator solution were used in the test solution and A c.c. of indicator solution of the same concen-tration were required to match the colour of the alkali solution with that produced in the test solution, then of the T c.c. an amount equivalent to A c.c. must have been in the alkaline or anion form, and therefore the amount of neutralisation, x,

undergone by the indicator in the test solution was $\dfrac{T}{A}$. Hence

$$pH = pK_{HIn} + \log \frac{x}{1 - x}.$$

This equation was found to hold quantitatively for the α-, β- and γ-dinitrophenols and *para*- and *meta*-nitrophenols. Their values of pK_{HIn} for temperatures ranging from 5° to 50° C. are given in Table 56.

TABLE 56.

pK_{HIn} OF MICHAELIS' INDICATORS.

Temperature.	α-Dinitro Phenol.	β-Dinitro Phenol.	γ-Dinitro Phenol.	p-Nitro Phenol.	m-Nitro Phenol.
5° C. . .	4·13	3·76	5·21	7·33	8·43
10° C. . .	4·11	3·74	5·18	7·27	8·39
15° C. . .	4·08	3·71	5·15	7·22	8·35
20° C. . .	4·05	3·68	5·14	7·16	8·31
30° C. . .	3·99	3·62	5·09	7·04	8·22
40° C. . .	3·93	3·56	5·04	6·93	8·15
50° C. . .	3·88	3·51	4·99	6·81	8·07

In order to make pH measurements over almost the complete pH range, Michaelis and Gyemant studied the colour changes of phenolphthalein and alizarine yellow, GG (salicyl yellow ; *m*-nitro-benzeneazosalicylic acid). They found, although the varying colour intensities were not strictly parallel with their extents of neutralisation as monobasic acids on account of their polyacidic nature and the closeness of their dissociation constants, that it was possible to calibrate the degrees of dissociation, x, found as with the nitrophenols, against pH values. Their data are recorded in Tables 57 and 58.

TABLE 57.

CALIBRATION OF PHENOLPHTHALEIN. TEMPERATURE 18° C. TEMPERATURE CORRECTION 0·011 $+ (t° - 18)$.

x.	pH.	x.	pH.	x.	pH.
0·01	8·45	0·16	9·1	0·55	9·8
0·014	8·5	0·21	9·2	0·60	9·9
0·030	8·6	0·27	9·3	0·65	10·0
0·047	8·7	0·34	9·4	0·70	10·1
0·069	8·8	0·40	9·5	0·75	10·2
0·090	8·9	0·45	9·6	0·80	10·3
0·120	9·0	0·50	9·7	0·845	10·4
—	—	—	—	0·873	10·5

TABLE 58.

CALIBRATION OF SALICYL YELLOW.

Temp. 20° C.

x.	pH.	x.	pH.	x.	pH.
0·13	10·0	0·36	10·8	0·75	11·6
0·16	10·2	0·46	11·0	0·83	11·8
0·22	10·4	0·56	11·2	0·88	12·0
0·29	10·6	0·66	11·4	—	—

The following table, Table 59, gives the ranges for which the Michaelis' indicators are applicable, and the suitable concentrations of the indicator solutions :—

TABLE 59.

PARTICULARS OF THE MICHAELIS' INDICATORS.

Indicator.	pH Range.	Solution.
2 : 4 Dinitrophenol (α) .	2·0–4·7	Saturated aqueous.
2 : 6 Dinitrophenol (β) .	1·7–4·4	0·05 % ,,
2 : 5 Dinitrophenol (γ) .	4·0–6·0	Saturated ,,
p-Nitrophenol . .	4·7–7·9	0·1 % ,,
m-Nitrophenol . .	6·3–9·0	0·3 % ,,
Phenolphthalein . .	8·5–10·5	0·04 %, 70 % water, 30 % alcohol.
Salicyl yellow . .	10·0–12·0	Diluted saturated alcoholic.

The pH ranges given in Table 59 appear to be somewhat too wide for accurate work, and Kolthoff (*Indicators*, p. 161) has found that the useful ranges of the indicators are less extensive. Thus, he suggests that with the α-, β-, and γ-dinitrophenols pH measurements should be made within the respective ranges : pH 2·6-4·4, 2·4-4·0, and 4·0-5·8 ; with p-nitrophenol from pH 5·6-7·6 ; with m-nitrophenol, pH 6·6-8·6 ; with phenolphthalein from pH 8·2 to pH 10·0 ; and with salicyl yellow the same range as that advocated by Michaelis. Kolthoff prepares the indicator solutions of slightly different concentrations. They are as follow : α-dinitrophenol, 0·1 per cent. dilute alcoholic solution ; β-dinitrophenol, 0·1 per cent. dilute alcholic solution ; γ-dinitrophenol, 0·1 per cent. dilute alcoholic solution ; p-nitrophenol, 0·3 per cent. aqueous solution ; m-nitrophenol, 0·3 per cent. aqueous solution ; phenolphthalein, 0·1 per cent. in

50 per cent. alcohol ; salicyl yellow, 0·1 per cent. alcoholic solution for the range *p*H 10 to 11, and 0·025 per cent. in 25 per cent. alcohol for the determination of *p*H values from 11 to 12.

This method can be made more rapid when a large number of *p*H determinations are to be continuously made. Michaelis and Gyemant point out that it is an easy matter to prepare a series of solutions containing increasing amounts of the various indicators in the coloured or so-called alkaline forms, such that the intensity of colour in one tube corresponds to a known *p*H under certain definite conditions of working, whilst that of the solution in the next tube to a *p*H value which is 0·2 *p*H higher, and so on. The

TABLE 60.

MICHAELIS' AND GYEMANT'S INDICATOR STANDARDS.

α-Dinitrophenol.

Diluted Indicator, c.c. .	0·51	0·78	1·20	1·74	2·5
*p*H	2·8	3·0	3·2	3·4	3·6
Diluted Indicator, c.c. .	3·4	4·6	5·7	6·7	—
*p*H	3·8	4·0	4·2	4·4	—

γ-Dinitrophenol.

Diluted Indicator, c.c. .	0·74	1·1	1·65	2·4	3·4
*p*H	4·0	4·2	4·4	4·6	4·8
Diluted Indicator, c.c. .	4·5	5·5	6·6	—	—
*p*II	5·0	5·2	5·4	—	—

p-Nitrophenol.

Diluted Indicator, c.c. .	0·16	0·25	0·4	0·63	0·94
*p*II	5·4	5·6	5·8	6·0	6·2
Diluted Indicator, c.c. .	1·4	2·0	3·0	4·05	—
*p*II	6·4	6·6	6·8	7·0	—

m-Nitrophenol.

Diluted Indicator, c.c. .	0·27	0·43	0·66	1·0	1·5
*p*II	6·8	7·0	7·2	7·4	7·6
Diluted Indicator, c.c. .	2·3	3·0	4·2	5·2	—
*p*II	7·8	8·0	8·2	8·4	—

concentrations of a series of these standard coloured solutions can easily be calculated for those indicators which behave as a mono-basic acid. The solutions given in Table 60 used by Michaelis and Gyemant constitute suitable standards. To 6 c.c. of solution under test 1 c.c. of the indicator solution is added and the colour produced matched with that of one of the standards. These may be prepared by running the calculated volumes of the various indicator solutions which have been diluted ten times into the test-tubes of standard size, and then making up the volume in each tube to 7 c.c. (the final volume employed of the test solution) with centinormal sodium hydroxide solution. The tubes are sealed with corks, carefully coated with paraffin wax to prevent the passage of cork-acids into the solutions, and when not in use stored in the dark.

These solutions are stated to retain their correct depths of colour for some months, but certain investigators have found the colours in the more alkaline solutions undergo change. The best results are to be obtained using freshly prepared standards of comparison. To overcome this difficulty Kolthoff (*Indicators*, p. 164) has prepared a series of solutions, having comparable colours, from potassium chromate and potassium bichromate whose colours are permanent for upwards of a year. His solutions are prepared from 0·1 per cent. solutions of either K_2CrO_4 and $K_2Cr_2O_7$ and diluting to 10 c.c. The pH data corresponding to the various shades of colour are based on experiment. The data are given in Table 61 and were taken from Kolthoff's book. (See also *Pharm. Week.*, 1923, **60**.)

Michaelis, Gyemant and Krüger (*Biochem. Zeitsch.*, 1920, **109**, 165 ; 1921, **119**, 307) have investigated the errors which may be introduced into the determination of hydrogen-ion concentrations through the presence of neutral salts. For neutral salt concentrations up to 0·5 N, the error involved in the use of *p*-nitrophenol is negligible, but for the other indicators the pH values are approximately 0·1 pH unit too high when the concentration is 0·15 N ; and for 0·5 N salt concentration with either α-dinitrophenol, *m*-nitrophenol or phenolphthalein, the pH values are 0·2 pH too high, with β-dinitrophenol, 0·3 pH too high, and with γ-dinitrophenol the pH values are about 0·1 pH unit too high.

Alcohol has a very marked effect on the dissociation of electrolytes and especially of indicators. Michaelis and Mizutani (*Biochem. Zeitsch.*, 1924, **147**, 7) have determined the variations in the dissociation constants of the Michaelis' indicators caused by the varying alcohol contents of solutions. It is, of course, not

TABLE 61.

KOLTHOFF'S CHROMATE COLOUR STANDARDS FOR THE MICHAELIS INDICATORS. TEMP. 15° C.

$C.c.$ 0.1 % K_2CrO_4 in 10 c.c.	0.3	0.45	0.7	1.1	1.5	1.8	2.3	3.1	3.7	4.0
Colour similar to that produced at pH by: (a) 0.2 c.c., 0.1 % α-*Dinitrophenol* per 10 c.c.	3.0	3.2	3.4	3.6	3.8	4.0	4.2	4.4	4.6	—
(b) 0.2 c.c., 0.3 % p-*Nitrophenol* per 10 c.c.	(5.6)	5.7	5.8	5.9	6.1	6.2	6.5	6.8	7.1	7.2
(c) 0.1 c.c. ditto	—	—	—	—	—	7.1	7.4	7.6	—	—

$C.c.$ 0.1 % $K_2Cr_2O_7$ in 10 c.c.	0.23	0.35	0.55	0.72	1.1	1.55	1.8	2.2	3.0
Colour similar to that produced at pH by: (a) 0.2 c.c., 0.1 % γ-*Dinitrophenol* per 10 c.c.	4.0	4.1	4.3	4.5	4.7	4.9	5.1	5.3	5.5
(b) 0.4 c.c., 0.3 % m-*Nitrophenol* per 10 c.c.	7.0	7.2	7.5	7.7	7.9	8.1	8.3	8.5	—
(c) 0.2 c.c., 0.05 % *Salicyl yellow* per 10 c.c.	—	—	—	(9.8)	10.2	10.5	10.6	10.8	11.3
(d) 0.2 c.c., 0.025 % *Salicyl yellow* per 10 c.c.	—	—	10.2	10.4	10.8	—	—	—	—

possible to attach any real meaning to pH values of aqueous-alcoholic solutions, but their determination may occasionally furnish a convenient method of control. As it was not possible to obtain alcohol-water solutions of known hydrogen-ion concentration, they standardised their hydrogen electrode measurements of these solutions against those given by the electrode in aqueous solutions of known pH values. The variations in pK$_{\text{HIn}}$ of the nitrophenol indicators are given in Table 62

Table 63 shows that the increasing alcohol contents depressed the ionisation of the indicators. The pH values of alcoholic solutions may be determined with the aid of the indicators given in Table 62 and the appropriate pK$_{\text{HIn}}$ values by the Michaelis method, with the modification that the colour is developed in the comparison solutions, which must have the same alcohol content as the solution under examination, by means of N/100—NaOH

TABLE 62.

VALUES OF pK$_{HIn}$ OF THE MICHAELIS INDICATORS IN AQUEOUS
ALCOHOLIC SOLUTIONS.

	pK$_{HIn}$ at Alcohol Contents (Per Cent. Volume].									
	0 %.	10 %.	20 %.	30 %.	40 %.	50 %.	60 %.	70 %.	80 %.	90 %.
m-Nitrophenol	8·37	8·56	8·75	8·97	9·15	9·40	9·64	9·92	10·24	10·73
p-Nitrophenol .	7·15	7·17	7·28	7·38	7·63	7·85	8·11	8·34	8·59	8·90
γ-Dinitrophenol	5·15	5·20	5·23	5·39	5·45	5·58	5·70	5·95	6·08	9·40
α-Dinitrophenol	4·00	4·00	4·00	4·00	4·00	4·15	—	—	—	—

for alcohol contents up to 70 per cent., and by N/10—NaOH
for contents from 70 per cent. to 100 per cent. The method may
also be used for work with phenolphthalein, using the data of
Michaelis and Mizutani given in Table 63.

TABLE 63.

RELATION BETWEEN pH AND THE DEGREE OF NEUTRALISATION,
x, OF PHENOLPHTHALEIN IN ALCOHOLIC SOLUTIONS.

x.	pH Values for Alcohol Contents (Percentage by Volume).										
	0 %.	10 %.	20 %.	30 %.	40 %.	50 %.	60 %.	70 %.	80 %.	90 %.	95 %.
0·01	8·5	8·7	8·9	9·2	9·5	9·8	10·2	10·6	10·8	11·1	11·3
0·02	8·6	8·8	9·0	9·3	9·7	10·0	10·4	10·7	11·0	11·2	11·5
0·04	8·8	8·9	9·2	9·5	9·9	10·2	10·6	10·9	11·2	11·4	11·7
0·06	8·9	9·0	9·4	9·7	10·0	10·3	10·7	11·0	11·3	11·6	11·8
0·08	8·98	9·1	9·5	9·8	10·1	10·4	10·8	11·1	11·4	11·7	11·9
0·1	9·04	9·2	9·6	9·8	10·2	10·5	10·9	11·2	11·5	11·8	12·0
0·2	9·22	9·4	9·8	10·1	10·5	10·8	11·1	11·5	11·9	12·1	12·3
0·3	9·38	9·6	9·9	10·2	10·6	10·9	11·3	11·7	12·1	12·3	12·4
0·4	9·54	9·7	10·1	10·4	10·8	11·1	11·4	11·8	12·2	12·4	12·6
0·5	9·70	9·9	10·2	10·5	10·9	11·2	11·5	12·0	12·4	12·6	12·7

Colorimetric Method using Standard Buffer Solutions.

In Chapter XI buffer mixtures are described whose pH values
have been accurately determined. If therefore we select a series
of these solutions, covering the pH range in which lie the pH values
of the solutions requiring examination, such that the buffer
solutions differ successively in pH by about 0·2, and place 10 c.c.
(say) of each in test-tubes of colourless glass and having the same
dimensions, and then carefully add a small equal quantity of a

suitable indicator for the particular pH range to each solution, we obtain a series of different colours corresponding to the different pH values. Hence, if we take the same volume, 10 c.c., of the test solution and add to it an equal volume of the indicator solution to that used in the buffer solutions, we obtain a colour which we may be able to match exactly with one of the coloured standard buffer solutions. If a complete match is found, then the test solution and the corresponding buffer solution will have the same pH value. If, however, a complete match has not been obtained but the colour of the test solution falls between those of two successive standards, then it is known that the desired pH value must lie between the pH values of the two standards. Hence, by choosing standards with pH values sufficiently close to one another the unknown pH value can be ascertained with a precision of 0·1 or 0·05 pH unit. It must be emphasised here that the indicator concentrations must be the same for all the solutions, and that the colours of the different solutions must be examined through the same thicknesses of the liquids. As we have seen the indicator concentration has an important bearing on the depth of colour of a one-coloured indicator. With a two-coloured indicator, the colour produced is the result of the ratio of indicator in the acid- and alkaline-forms, which remains constant at any given pH, and consequently the amount of indicator used is not then of such vital importance, though it will be appreciated that the difference in intensities of colour will render comparison difficult.

Selection of Indicator.

As a rule the most satisfactory range to employ an indicator for the determination of pH lies round about pH $= p$K$_{HIn}$, for it is in this region that the colours undergo their maximum change which facilitates colour-matching. This, however, only holds for those indicators whose acid and alkaline colours are of about the same intensity. If one form should happen to produce a deeper coloration than the other, then this will tend to cause the best pH range to be displaced towards the end where the deeper colour begins to assert itself. In the case of the sulphone-phthaleins the various alkaline colours are much more intense than the yellow acid forms, and this leads to more pronounced changes in colour occurring during the first halves of the neutralisation. Saunders (*Proc. Camb. Phil. Soc.*, 1923, **1**, 31) found that for bromo-cresol purple the best range was from pH 5·8 to pH 6·4, pK $=$ 6·3 ; bromothymol blue, pH 6·4–7·2, pK $=$ 7·1 ; phenol red, pH 7·1–7·9, pK $=$ 7·7 ; cresol red, pH 7·65–8·45, pK $=$ 8·1 ;

and for thymol blue, pH 8·4–9·2, pK = 8·8. He claims that measurements can be made within these ranges having an accuracy of 0·01–0·02 pH unit. This must be regarded as exceptional accuracy for colorimetric estimations. Indicators, having wide transition intervals usually exhibit a very gradual change in colour, tending to make colour-matching difficult and the accuracy poor, *e.g.*, litmus. The choice of indicators should be guided by considerations of this kind rather than by the desire to use the minimum number of indicators to span the entire pH range.

In selecting an indicator for any given determinations, the most appropriate indicator for the purpose should be used. This may be done by means of either preliminary tests with several indicators or a mixed indicator. If the former method of orientation be used, it is only necessary to add a few drops of the indicators to different portions of the solution until it is found that its pH lies somewhere between the pH values corresponding to the colour changes of two indicators whose pK's are close to one another. An approximate idea of the unknown pH value may be obtained by adding a few drops of a mixed indicator, of which there are several now on the market.

" Universal " or Mixed Indicators.

It may be as well to include a few notes on the preparation of mixed indicators. Two will be described.

Bogen (*J. Amer. Med. Assoc.*, 1927, **89**, 199) has recently introduced the following, whose colours range from red to blue in the order of the spectrum for pH values varying from pH 2 to pH 10. In 500 c.c. of absolute alcohol, 0·1 gram of phenolphthalein, 0·2 gram of methyl red, 0·3 gram of dimethylaminoazobenzene, 0·4 gram of bromothymol blue, and 0·5 gram of thymol blue are dissolved and then sufficient sodium hydroxide is added to produce a yellow colour. Amounts of from 1 drop to 1 c.c. may be used. At pH 2 its colour is red ; at pH 4, orange ; at pH 6, yellow ; at pH 8, green ; and at pH 10 blue.

Another mixed indicator covering a pH range from 3 to 11 has been described by Fairbrother (*Industrial Chemist*, 1928, **4**, 96). It is prepared by dissolving 0·04 gram of methyl orange, 0·02 gram of methyl red, 0·12 gram of α-naphthol-phthalein, and 0·08 gram of phenolphthalein in 100 c.c. of 70 per cent. alcohol. The following colours are obtained with increasing pH red, orange, yellow, green, blue, violet, reddish violet.

For the colorimetric determination the most suitable indicator should be chosen from Table 53. There is a tendency nowadays

to use those of Clark and Lubs and Cohen on account of their
brilliant colour changes.

Preparation of Indicator Solutions.

(1) *Clark and Lubs' Indicators.*—In regard to the sulphone-
phthaleins it is essential that the purest products should be used,
for with impure samples difficulty may sometimes be experienced
in getting them into aqueous solution. It is probably for this
reason that several workers have resorted to the use of alcohol.
Clark and Lubs prefer aqueous solutions which they prepare in
the following manner : 0·1 gram of the dry powder is ground in
an agate mortar with the stoichiometrical amount of N/20–
NaOH, Table 64, to form the sodium salt, and the solution thus
formed is diluted with water to 25 c.c.   This gives a 0·4 per cent.
solution which is put aside as a stock solution, and which they
dilute to either 0·04 per cent. or 0·02 per cent. for use.   For
ordinary purposes, about 5 drops of indicator should be added
to 10 c.c. of solution.

TABLE 64.

CLARK AND LUBS' INDICATORS.

Indicator.	Mol. Wt.	C.c. N/20— NaOH to 0·1 gm. solid.	Concentration per Cent.
Thymol blue . . .	466	4·3	0·04
Bromophenol blue . . .	669	3·0	0·04
Methyl red	269	7·4	0·02
Bromocresol purple . .	540	3·7	0·04
Bromothymol blue . . .	624	3·2	0·04
Phenol red	354	5·7	0·02
Cresol red	382	5·3	0·02
Cresol-phthalein . . .	—	—	0·02

Kolthoff, however, prefers to prepare the sulphone-phthalein
indicators by dissolving 0·1 gram in 20 c.c. of warm alcohol and
then diluting to 100 c.c. with water.

(2) For the majority of the ordinary indicators, the solution
should contain about 0·1 per cent. of the indicator.   Soluble
indicators, *e.g.*, methyl orange, methyl violet, Congo red, benzo-
purpurin, litmus (1 per cent. solution), salicyl yellow, tropæolin
O, and tropæolin OOO, are simply dissolved in water.   Many of
the indicators have first to be dissolved in alcohol and then diluted
with the requisite volume of water.   Thus 100 c.c. of each of the
following indicator solutions should contain approximately : 0·1

gram of dimethylaminoazobenzene and 90 c.c. of alcohol, 0·2 gram of methyl red and 60 c.c. of alcohol, 0·1 gram of neutral red and 60 c.c. of alcohol, 0·1 gram of α-naphthol-phthalein and 50 c.c. of alcohol, 0·1–1·0 gram of phenol-phthalein and 60 c.c. of alcohol, 0·1 gram of thymol-phthalein in 100 per cent. alcohol, 0·2 gram of alizarine and 90 c.c. of alcohol, 0·5 gram of resolic acid and 50 c.c. of alcohol, and 0·1 gram nitramine and 60 c.c. of alcohol. Of these solutions volumes varying from 1 to 10 drops, which should be measured out from a graduated pipette and preferably not from a bottle, should be added to each 10 c.c. of the test solution.

The Comparator.

The matching of the colour of a test solution, to which the correct amount of indicator solution has been added, with that produced in a buffer solution of known pH, may be carried out directly, merely by arranging the coloured buffer solutions in the alternate holes of a test-tube stand in the order of pH, and then to move the solution undergoing examination from hole to hole until the position is found such that its colour is seen to fall between those of two consecutive buffer solutions. Suitable illumination is necessary and the comparison is facilitated if a white background is placed behind the test-tube stand. It is often an advantage to have the tubes inclined at a small angle to the vertical so that the solutions may be viewed through a greater depth of liquid. As mentioned above, it is imperative that the concentrations of the indicator in all the solutions should be the same, and moreover, that the same thickness of the various solutions should be compared.

Dichromatism of the Sulphone-phthaleins.

A difficulty encountered in matching the colours of certain of the sulphone-phthalein indicators is that of " dichromatism." In other words, a solution when viewed through one thickness appears to have one colour whereas when examined through another may appear to have quite a different colour. This is the case with bromophenol blue and bromocresol purple. So far we have regarded the colours of solutions as if they were separate entities. Strictly speaking, we should consider the colour of each solution in terms of its absorption spectrum and of the changes in the intensities of the light radiations which it allows to be transmitted. It is the relative intensities of the transmitted waves which determine the colour sensation, or the colour which the solution will

appear to have. The extent of the absorption of light waves is determined, not only by the wave-lengths, but by the width of the solution layer and the concentration of the solution. These factors will also determine the proportion of light transmitted through the solution. The intensities of the colour radiations after travelling through a liquid will be a function of the intensities of the respective radiations before entering the liquid. It is well known that the intensities of the many colour radiations which make up ordinary solar " white " light are very different from one another. They differ also from those emitted by hot bodies, *e.g.*, an electric filament, an electric arc or an incandescent gas burner. Hence the solar and artificial " white " lights are quite different from one another, as is exemplified by the appearance of the colours of articles when examined under their illumination. Ordinary daylight is rich in blue, whereas the light emitted by an electric carbon filament may be compared with light corresponding to the red end of the spectrum and relatively weak in blue radiations. The attempt to imitate daylight in modern electric lamps is effected by absorbing some of the red by means of a blue bulb. It happens that the absorption spectrum of bromophenol blue in its alkaline form has a large band in the yellow and the green, with the consequence that the transmitted light is made up almost entirely of red and blue light. Hence, such a solution would appear blue in daylight on account of its greater intensity of blue, whilst in the light from an electric carbon filament lamp with its preponderance of red it will appear red.

The cause of the different colours seen through different thicknesses of solution has been very neatly explained by Clark (*Determination of Hydrogen Ions*, 1923, p. 65). For simplicity, consider that the colour of a bromophenol blue solution seen by transmitted light is composed of red and blue, and that the intensities of these two kinds of radiations in the incident light are I_r and I_b respectively. Suppose that a_r and a_b are their respective " transmission coefficients " through the solution, *i.e.*, the ratios of the intensities of the incident beam and that transmitted light through unit thickness. Hence the intensity of the transmitted red light through unit thickness will be $I_r \times a_r$, and that of blue will be $I_b \times a_b$. After traversing a thickness, x, the intensities become

$$I_r \times a_r^x \text{ and } I_b \times a_b^x.$$

Although the actual values of these two expressions have not been determined, their importance will be understood by assuming that the intensity of the incident blue is 100, and of the red 30,

and that $a_b = 0.5$ and $a_r = 0.8$. When $x = 1$, $I_b \times a_b^x = 50$ and $I_r a_r = 24$, and therefore the blue colour will predominate. If, however, $x = 10$, $I_b \times a_b^x = 0.01$ and $I_r \times a_r^x = 0.30$, and thus the solution will appear red. Hence a solution may appear blue through a thin layer, but may appear red when viewed through thicker layers. The effect of varying the intensities of the incident radiations will be to alter the colours of the solutions. Thus if we interchange the numerical values taken in the above calculations, *i.e.*, let $I_r = 100$ and $I_b = 30$, then we find that for unit thickness, $x = 1$,

$$I_b \times a_b = 15 \text{ and } I_r \times a_r = 80,$$

and consequently the solution will now appear red, instead of blue as in the previous case.

Kolthoff calls attention to the different effect which buffer solutions may have on the " transmission-coefficients " compared with that of the solution undergoing examination, and so may cause the colours corresponding to the same pH value of different solutions to be in no way similar. He found that the dichromatism of bromophenol blue and other sulphone-phthaleins could be entirely eliminated by the use of alcohol or acetone. Due to this, the transition colours of bromophenol blue from yellow to blue in alcohol or dilute alcoholic solutions are quite different from those exhibited by aqueous solutions.

The Walpole Comparator.

Should the test solution be either slightly coloured or turbid, then the direct method of matching its colour obtained by the addition of indicator with that of a clear standard buffer solution will no longer be applicable. If the colour effects which give rise to the resulting colour are additive, then the colour seen by transmitted light through equal, superimposed, thicknesses of a clear buffer solution with added indicator and having the same pH as the test solution and of the test solution without indicator, should be the same as that observed when the same light passes through the same thickness of pure water and then through an equal thickness of the test solution having the same concentration of indicator as the standard buffer solution. This is the principle of the Walpole comparator and the so-called block comparator. Fig. 54 represents a section of Walpole's apparatus (*Biochem. Jour.*, 1910, **24**, 40). The interior is painted black. The various liquids are placed in the four plane bottom cells to the same depth in each. Light is made to pass up through these liquids, either by means of a reflector or reflecting surface or by some suitable direct illumination

placed underneath the apparatus. The cell containing a standard buffer and indicator is replaced by others until a perfect match is obtained. A modified form of this apparatus has been designed by Biehler (*Zeitsch. physiolog. Chem.*, 1910, **110,** 298). In this type of comparator the two pairs of solutions are seen through a uniform depth and consequently the observed colours are uniform. In the block comparator of Hurwitz, Meyer and Ostenberg testtubes are filled with various liquids and the colours observed through pairs, one placed behind the other (*Proc. Soc. Exp. Biol. and Med.*, 1915, **13,** 24). Equal depths of liquid obtain when viewed through the middle, and it is therefore in this portion of the pairs of tubes that the colours should be compared and ultimately matched. Figs. 55 and 56 refer to this type of comparator. The tubes are placed in blackened holes bored into a block of wood, and the colours observed through each of the three pairs of tubes through the rectangular slots provided. In A (Fig. 56) and C samples of the solution undergoing examination are placed, while in D and F are inserted standard buffer solutions containing indicator and differing by about 0·2 *p*H. Another portion of the test solution is placed in B together with the same concentration of indicator as in D and F, *viz.*, a definite volume for each 10 c.c., and the colour of this is modified by the tube of distilled water in E. The standard coloured buffer solutions in D

FIG. 54.—Walpole Comparator.

FIG. 56.—Arrangement of Tubes in the Comparator.

and F are changed until a pair is found giving colours between which the colour of the unknown solution, when viewed in the direction of the arrow, is found to lie.

FIG. 55.—The B.D.H. Comparator Case.
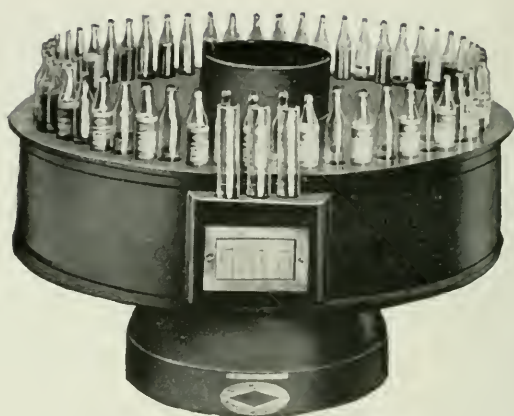
Fig. 57.—La Motte Roulette Comparator.
[*See page* 229.
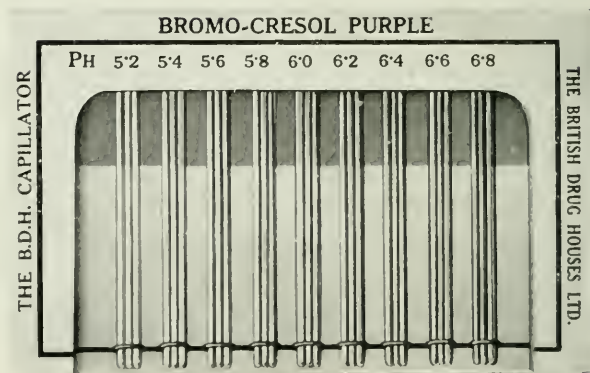
Fig. 58.—The B.D.H. Capillator.
[*See page* 230.

The determination of hydrogen-ion concentrations by this device is rendered very much more rapid if a series of buffer standards containing measured amounts of suitable indicators are available for pH intervals of about o·2 pH. These may be prepared in glass tubes which are not attacked and by using only those indicators which give colours that remain unchanged over long periods. Such solutions should be preserved in sealed tubes and kept out of the light except when in use. If sealing is effected with corks, the corks must be carefully coated with a paraffin wax to prevent the passage of any of the acids contained in cork into the buffer solutions. Convenient ranges of these coloured standards are now procurable commercially and are guaranteed for a year. Table 65 gives those indicators which are suitable for the purpose. Nevertheless, the standards should be continually checked, and preferably pH measurements should be made using two sets of colour standards prepared from different indicators.

TABLE 65.

INDICATORS SUITABLE FOR USE IN COMPARATORS AS PERMANENT COLOUR STANDARDS.

Metacresol purple	.	.	.	.	$\begin{cases} \text{o·5–2·5} \\ \text{7·6–9·2} \end{cases}$	red—yellow yellow—violet
Thymol blue	.	.	.	.	$\begin{cases} \text{1·2–2·8} \\ \text{8·0–9·6} \end{cases}$	red—yellow yellow—blue
Bromophenol blue	.	.	.	.	3·0–4·6	yellow—violet
Methyl orange	.	.	.	.	3·1–4·4	red—yellow
Ethyl orange	.	.	.	.	3·5–4·5	red—orange
Benzene-azo-α-naphthylamine		.	.	3·5–5·7	red—orange
Bromocresol green	.	.	.	.	4·0–5·6	yellow—blue
Chlorophenol red	.	.	.	.	5·0–7·0	yellow—violet red
Bromocresol purple	.	.	.	.	5·2–6·8	yellow—violet
Bromothymol blue	.	.	.	.	6·0–7·6	yellow—blue
Neutral red	.	.	.	.	6·8–8·0	red — yellow
Phenol red	.	.	.	.	6·8–8·4	yellow—red
Cresol red	.	.	.	.	7·2–8·8	yellow—violet red
Thymol blue	.	.	.	.	8·0–9·6	yellow—blue

An improved comparator, known as the " Roulette Comparator," is made by the La Motte Chemical Products Co. of Baltimore, U.S.A., with which pH measurements can be made rapidly and under excellent conditions of illumination. A picture of the apparatus is given in Fig. 57. It comprises a stationary base and a metal band, inside which a wooden drum revolves on ball bearings. Illumination is provided by a 40 watt Mazda lamp fixed in the centre of the base. A piece of " Dalite " glass is placed in the back of the block between the three test tubes and the colour

standards, and a piece of etched glass is placed on the outside of
the block directly over the three slots.   To operate the comparator
three sets of tubes of colour standards, covering the pH range of
the solutions to be tested, are placed in pH order in the alternative
holes of the revolving drum.   Tubes of the same bore, filled with
distilled water, are inserted in the vacant holes.   Suppose the
required pH range is pH 5-9.   Sets of standard buffer solutions
coloured with chlorophenol red, pH 5·2-6·8 ; bromothymol blue,
pH 6·0-7·6 ; and phenol red, pH 6·8-8·4 might therefore be
used.   If the pH of the solution being tested lies with the range of
bromothymol blue, fill three of the test-tubes to the mark, 10 c.c.,
and place them in the three holes in the block.   After adding
the requisite amount of bromothymol blue to the middle tube, and
shaking, the light is switched on and the drum revolved until the
bromothymol blue standards are directly behind the test sample.
Looking toward the electric bulb through the three slots in the
block, slowly revolve the drum until the colour seen through the
central test tube exactly matches that of one of the tubes on either
side of it, or else lies between them.   The pH value can then be
read off directly from the labelled colour standards.

Micro-Colorimetric Methods.

Occasionally the amounts of the samples to be tested are so
small as not to permit of the application of the foregoing methods.
Micro methods have been introduced, of which two will now be
discussed : (a) spotting, and (b) using the capillator.

(a) Spotting.—Felton (*J. Biol. Chem.*, 1921, **46,** 299) places
a drop of the liquid on a porcelain or " opal " glass plate and mixes
with it an equal drop of a suitable indicator.   The colour is com-
pared with those given by the same treatment of buffer solutions
of known pH values.   The drops must be accurately measured.
(*Cf.* Myers, Schmitz, and Booker, *J. Biol. Chem.*, 1923, **57,** 209,
and Brown, *Chem. Abs.*, 1924, **18,** 1135.)

(b) Using Capillator.—The capillator, as supplied by Messrs.
The British Drug Houses, Ltd., and illustrated in Fig. 58, was
designed by Ellis, Brit. Patent 235,458, 1924.   It consists of a series
of capillary tubes filled with buffer solutions containing an indicator.
These tubes are mounted, three together, on a white card, and
form a series of coloured strips, each strip being marked with
its exact pH value.   Each card illustrates the complete colour
change of the indicator.

A slot is provided in the card, so that, by holding it up, colour
comparisons may be made by transmitted light, whereas by viewing

against the white background of the card comparisons may be made by reflected light.   The whole series of colours being visible all the time, the actual colour-matching can be carried out very quickly.

A determination of pH is carried out by using a capillary tube as a pipette and measuring by this means equal quantities of the liquid and indicator, mixing the two in a small watch glass and then drawing the mixed liquids back into the capillary tube.   The colour of the mixed liquids is then matched against the capillator standards.

Imitation Indicator Colour Standards.

There have been recently several attempts to prepare solutions of different colours which match exactly the colours established by certain indicators in buffer solutions of different pH values. In order that the solutions might be stable, and therefore their colours, attention has been directed to inorganic salt solutions. Actually, to secure an inorganic salt solution of exactly the same colour as that of indicator dye solution is almost impossible, but it must be conceded that very many satisfactory imitations have been prepared, and which may be of appreciable use as colour standards.   Taub (*J. Amer. Pharm. Assoc.*, 1927, **16,** 116) has prepared 73 such solutions of mixtures of salts of copper, iron and copper, and which may be substituted for indicator colour standards corresponding to pH values varying from pH 1·2 to pH 9·0. Kolthoff (*Pharm. Weekblad*, 1922, **59,** 104) found that the colours obtained by mixing a solution containing 45·05 grams of $FeCl_3$, $6H_2O$ in 1 litre of 1 per cent. hydrochloric acid with another solution made up of 72·8 grams of $Co(NO_3)_2,6H_2O$ per litre of 1 per cent. hydrochloric acid solution in various proportions closely resembled those given by adding 0·2 c.c. of a 0·05 per cent. indicator solution to a buffer solution (10 c.c.) at the pH shown in Table 66, in the case of neutral red, methyl orange and methyl red, and 0·2 c.c. of a 0·1 per cent. tropæolin OO solution.

The search for really satisfactory inorganic colour standards will necessitate increased attention being given to the absorption spectra and the transmittancies of light of varying wave-lengths of salt solutions.   This may eventually show the way by which absorption spectra of solutions of mixtures of inorganic salts may be obtained that compare favourably with those given by some particular indicator solution at a definite pH value.   Work of the type recently done by Mellon and Martin (*J. Physical Chem.*, 1927, **31,** 161) on the spectral transmission curves of aqueous

solutions of ordinary indicators and of inorganic salts may prove to be extremely useful. It is possible that a series of coloured glasses might serve as standards.

TABLE 66.

KOLTHOFF'S IMITATION COLOUR STANDARDS.

Solution : To 10 c.c. Co(NO$_3$)$_2$ add c.c. of FeCl$_3$.	pH Values corresponding to			
	Neutral Red.	Methyl Red.	Methyl Orange.	Tropæolin OO.
0	—	5·2	3·1	2·0
1	7·0	—	3·2	—
3	7·1	5·3	3·5	2·1
5	7·2	5·5	3·7	2·2
7·5	7·4	5·6	3·9	2·3
10	7·6	5·6	4·0	2·3
15	7·8	5·7	4·2	2·4
20	7·9	5·8	4·3	2·5
30	—	5·8	4·5	2·5

Spectrophotometric Method.

Brode (*J. Amer. Chem. Soc.*, 1924, **46**, 581) has found that, with few exceptions, *e.g.*, methyl violet, the change in the hydrogen-ion concentration of a solution containing an indicator (*e.g.*, phthalein- and azo-dyes) does not shift the absorption bands as regards wave-length, but merely changes the intensity of absorption. He found that by comparing the intensities of absorption in the absorption bands in a solution of unknown pH with those in a standard buffer containing the same indicator, the pH value could be calculated. For this purpose the most suitable indicators covering the pH range 1 to 10 are thymol blue, a mixture of methyl red and bromothymol blue. Holmes (*J. Amer. Chem. Soc.*, 1924, **46**, 627) made similar observations with one- and two-colour indicators. With two-colour indicators, however, he showed that the ratios of the absorption intensities at two wave-lengths selected at or near the respective maxima of two absorption bands varied with the pH value of the solution. Thus for phenol-sulphone-phthalein he measured with the spectrophotometer the intensities of the absorption at 460 $\mu\mu$ and 560 $\mu\mu$ respectively. By constructing a calibration curve connecting the ratio of such intensities with pH values, he was able to read off unknown pH values once the value of the ratio had been found. Holmes and Snyder (*J. Amer. Chem. Soc.*, 1925, **47**, 221, 226) studied the dissociation curves of

thymol blue in alkaline solution and of bromocresol green by this method and found them to conform with the theoretical formula between 10 per cent. and 90 per cent. neutralisation. So also did thymol blue up to the point of half-neutralisation, but thereafter the dissociation of the indicator appeared to be retarded. They used the method for standardising α-naphthol 2-sulphonate indophenol as an indicator for use in the Gillespie " drop-ratio " method, $pK_{HIn} = 8.63$, pH range 7·6-9·6 (*J. Amer. Chem. Soc.*, 1925, **47**, 2232). Vlès (*Comp. rend.*, 1925, **180**, 584) endeavoured to avoid the tedious empirical calibration which the method involves, and derived an expression based on the absorption constants of the two tautomeric forms, the absorption ratio of the test solution, and the ionic dissociation of the indicator, by which if the pH values were not extremely small, he was able to calculate pH values correct to the first decimal place. Crystal violet and methyl red were anomalous.

Highly Coloured and Turbid Solutions.

Apart from the more satisfactory electrometric methods for the determination of pH values of those solutions which are either so turbid or so highly coloured that to interfere seriously with the colorimetric methods just described, two modifications of the colorimetric method seem to have been attempted. One, which is available for solutions which are highly buffered, is to dilute with distilled water until the colour or turbidity has become suitably diminished. That dilution can have very little effect, if any, on the hydrogen-ion concentration of well-buffered solutions will be apparent from Chapter X. The assumption is taken for granted by biochemists in their investigations of body fluids such as blood and urine, by bacteriologists and by soil-chemists with the so-called " soil solutions."

The second method, which is due to Sørensen, is to add to the standard buffer solutions amounts of a dye which exactly reproduce the colour of the test solution and then to proceed in the usual way with indicators.

CHAPTER XIII.

ERRORS IN INDICATOR METHODS AND THE USE OF INDICATORS IN TITRATIONS.

Apart from the ordinary manipulative errors, there are a number of errors which are inherent in the various indicators themselves. They are (1) errors introduced by the dissociation of the indicator as either an acid or a base in supplying hydrogen-ions to the test solution, the " acid error " ; (2) errors due to the action of neutral salts which may be present in a solution upon the colour and the incidence of the colour change, the " salt error " ; (3) errors through the interaction of an indicator with ampholytic bodies such as proteins and certain inorganic hydroxides, the " protein error " ; (4) errors due to effect of temperature upon the indicator dissociation ; and (5) errors caused by the presence of alcohol.

The " Acid Error."

As indicators function either as weak acids or bases, it is obvious that in the minute concentrations used in test solutions they can have no appreciable effect upon the hydrogen-ion concentration of those solutions which are well buffered. If, however, the solution contains no buffering agents, then, according as the dissociation constant of the indicator is sufficiently great to enable it to affect the hydrogen-ion concentration of the solution, will there be introduced a difference between the observed and actual pH values. It is quite an easy matter to get some idea of the magnitude of the error from a knowledge of the dissociation constant of the indicator, the value of K_w, and the indicator concentration imparted to the solution. The error may become considerable when the pH of an unbuffered solution, $e.g.$, a very dilute alkali solution, is greater than pK_{HIn}. Thus a solution of alkali of about pH 10 would appear to have a value somewhere about pH 8-9 when examined with phenolphthalein. The use of two indicators of widely different constants will indicate the existence of such an error.

The "Salt Error."

The fact that organic substances can sometimes be forced out of an aqueous solution by the addition of common salt suggests that a neutral salt has some effect on the organic compound when the amount of added salt is inadequate to cause the separation from the solution.   In the case of indicators, it should be understood that many have very restricted solubility in aqueous solutions, so that the presence therein of salts may have relatively large effects on their behaviour.   In some cases, neutral salts cause a variation in the colour changes and also in the pH values at which these changes normally occur.   It is probable that the salt influences the ionic equilibria involved in the functioning of an indicator and that it has different effects on the two so-called acid and alkaline forms, which are here considered to be responsible for the colour produced by the indicator.   As suggested by Kolthoff, neutral salts may have some effect on the optical absorption of the two forms of the indicator.

Numerous investigators have measured the salt errors of the various indicators, and in so doing have compared their colours with those produced by the indicators in standard buffer solutions, which themselves have often contained free salts and thereby have given rise to additional errors.   The phthalate buffer solutions of Clark and Lubs cause certain indicators to precipitate, $e.g.$, methyl violet. With the majority of the common synthetic indicators the apparent error due to neutral salts does not exceed 0·2 pH unit.   As a general rule, it is more satisfactory for a worker first to standardise the behaviour of his indicators under the conditions prevailing in his solutions against the hydrogen electrode, and so get some estimate of the errors which may be introduced.   Very often, the " salt error " of an indicator is studied in regard to its behaviour in the presence of alkali metal salts.   In actual practice, the salts encountered are often very different.   Unless a worker bases his colorimetric measurements directly on electrometric data gained from a preliminary examination of the type of solutions with which he has to deal, he should always be on the watch for any anomalies especially when the solutions contain any salts that may affect his results.   It is to avoid the introduction of such errors that the use of two indicators has been recommended.   Numerous researches have been directed to the evaluation of the salt errors of particular indicators by Sørensen, Palitzsch, Szyskovski, Kolthoff, Saunders, McClendon, and others.   In the opinion of the author, it would be of little value to attempt to summarise their conclusions, but in order to give some idea of the magnitude of the salt errors of

the common indicators, Tables 67 and 68 are inserted. These were taken from Kolthoff (*Rec. trav. Chim.*, 1922, **41**, 54 ; 1925, **44**, 275), and Saunders (*Proc. Camb. Phil. Soc.*, 1923, **1**, 31).

TABLE 67.

SALT ERRORS OF INDICATORS.

Indicator and Salt.	Neutral Salt Concentration.				
	1·0 N.	0·5 N.	0·25 N.	0·2 N.	0·1 N.
Tropæolin OO—KCl .	+ 0·23	+ 0·06	− 0·01	—	− 0·05
Thymol blue, pH 1·2-2·8 KCl.	+ 0·05	− 0·04	—	− 0·06	− 0·06
Methyl orange—KCl .	+ 0·23	+ 0·02	− 0·08	—	− 0·08
Methyl yellow—KCl .	—	—	—	—	− 0·08
Bromophenol blue—KCl	− 0·35	− 0·35	− 0·15	—	− 0·05
,, ,, —NaCl	− 0·35	− 0·27	—	—	− 0·15
Congo red—NaCl .	− 0·9	− 0·55	—	− 0·25	0
Bromocresol purple—NaCl.	—	− 0·25 (0·6 N)	—	—	—
Bromothymol blue—NaCl.	—	− 0·19 (0·6 N)	—	—	—
Methyl red—NaCl .	—	+ 0·1	—	—	—
p-Nitro-phenol—NaCl .	—	− 0·05	—	—	—
Azolitmin—NaCl . .	—	− 0·55	—	—	—
Phenol red—NaCl .	—	− 0·15	—	—	—
Neutral red—NaCl .	—	+ 0·12 (0·6 N)	—	—	—
Cresol red—NaCl .	—	− 0·20	—	—	—
Brilliant yellow—NaCl .	—	0·0	—	—	—
Phenol-phthalein—NaCl	—	− 0·17	—	—	—
Thymol blue, pH 8·0-9·6 NaCl.	—	− 0·17	—	—	—
Nitramin—KCl . .	− 0·16	− 0·10	− 0·10	—	− 0·06
Tropæolin O—NaCl .	+ 0·62	+ 0·53	+ 0·44	—	+ 0·38

The " salt errors " of Congo red, tropæolin O, azolitmin (litmus) and of bromophenol blue in the higher concentrations of neutral salts given in Table 67 show that these indicators are unsatisfactory for colorimetric work. The errors of the remaining indicators listed in Table 67 reveal that in normal circumstances they may be expected to behave satisfactorily, for their errors are seen to be negligible for ordinary solutions. Their salt errors only become large with increasing salt concentration. The errors given in Table 68 are remarkable in that they show that pH values, determined colorimetrically on the grounds that the salts included in Clark's buffer solutions do not influence the colours of the several indicators, are also affected by very small concentrations of electrolytes. Certain indicators, particularly chlorophenol red,

bromocresol green and phenol red, give large errors in the presence of very small salt concentrations, whilst α-naphtholphthalein,

TABLE 68.

SALT ERROR OF INDICATORS AT LOW ELECTROLYTE CONCENTRA-
TIONS IN RELATION TO CLARK'S BUFFER SOLUTIONS.

Total Electrolyte Concentration.	Thymol blue.	Phenol-phthalein.	α-Naph-tholphtha-lein.	Phenol red.	Cresol red.	Neutral red.	Bromo-thymol blue.
0·001 N	+ 0·25	+ 0·25	+ 0·18	+ 0·35	+ 0·17	− 0·09	+ 0·19
0·005 N	+ 0·19	+ 0·19	+ 0·14	+ 0·28	+ 0·15	− 0·04	+ 0·17
0·01 N	+ 0·13	+ 0·14	+ 0·10	+ 0·22	+ 0·12	0·00	+ 0·15
0·02 N	+ 0·05	+ 0·06	+ 0·00	+ 0·15	+ 0·09	0·00	+ 0·12
0·03 N	—	—	—	+ 0·09	+ 0·07	0·00	

	Chloro-phenol red.	Bromo-cresol purple.	Bromo-cresol green.	Methyl red.	Alizarine.	Methyl orange.	Bromo-phenol blue.
0·001 N	+ 0·47	+ 0·13	+ 0·45	+ 0·17	+ 0·25	− 0·15	+ 0·25
0·005 N	+ 0·3	+ 0·10	+ 0·24	+ 0·10	+ 0·18	− 0·07	+ 0·20
0·01 N	+ 0·21	+ 0·09	+ 0·16	+ 0·06	+ 0·12	− 0·06	+ 0·17
0·02 N	+ 0·15	+ 0·08	+ 0·10	+ 0·03	+ 0·10	− 0·04	+ 0·15
0·03 N	+ 0·09	+ 0·07	+ 0·07	0·00	+ 0·06	− 0·02	—

cresol red, neutral red, methyl red, methyl orange, bromothymol blue and bromocresol purple in possessing small errors appear to be most serviceable for such solutions.

The "Protein Error."

This error is only likely to arise with physiological liquids and certain technical solutions such as those obtained in the leather, cereal and brewing industries. Proteins and their decomposition products are, besides being colloidal, amphoteric. They may, therefore, interact with acidic and basic indicators and in consequence the indicators may become partially adsorbed, and thus affect the colour. This is especially true of indicators that are colloidal. Thus, Congo red, which might be regarded as a colloidal electrolyte, is useless for solutions containing proteins. Azo-dye indicators are generally useless, though the protein error of methyl red is often very small. This was observed by Palitzsch (*Comp. rend. Lab. Carlsberg*, 1911, **10**, 162) when the pH values of the various protein solutions were about pH 5, but in more acid solutions, *ca.* pH 4, the indicator colours corresponded with values *ca.* pH 5.

Similar observations have been made by Kent-Jones (see p. 443) in connexion with the hydrogen-ion concentrations of aqueous extracts of flour. Good agreement between the electrometric and colorimetric pH values were obtained above pH 5·5, but between this value and pH 5·0 discrepancies just became apparent, the indicator always indicating a higher pH value. At pH 5·0 errors as high as 0·15 were found by the colorimetric method, whilst below the error became more and more marked, depending upon both the protein content and its nature. Hence, colorimetric methods in solutions of proteins are of doubtful worth, and electrometric methods should be employed.

The Temperature Effect.

An increase in temperature has a marked effect on electrolytic dissociation. It is well known that water, acids and bases, and therefore indicators, undergo enhanced ionisation. In other words K_w, the ionic product of water, and the constants of acids and bases, $viz.$, K_a and K_b, become larger, so that pK_w, pK_a and pK_b assume lower values. The chief effect of this is to diminish (a) the pH scale, (b) the pH corresponding to neutrality, and (c) the limiting pH values of the various indicator transition ranges. Thus at 18° C., $pK_w = 14·2$; at 70°, 12·75 ; and at 100°, 12·2, and the hydrogen-ion concentration at neutrality at the respective temperatures are given by pH 7·1, pH 6·4, and pH 6·1.

TABLE 69.

EFFECT OF TEMPERATURE ON pH RANGES AND DISSOCIATION CONSTANTS OF INDICATORS.

Indicator.	pH Ranges at		pK_{HIn} at 18° $-pK_{HIn}$ at 70°.
	18° C.	100° C.	
Methyl violet	0·1–3·2	0·5–1·7	—
Thymol blue	1·2 2·8	1·2–2·6	0·4
Tropæolin OO	1·3–3·3	0·8–2·2	0·45
Methyl yellow	2·9–4·0	2·3–3·5	0·18
Methyl orange	3·1–4·4	2·5–3·7	0·3
Methyl red	4·2–6·3	4·0–6·0	0·2
p-Nitro-phenol	5·0–7·0	5·0–6·5	0·5
Phenol red	6·8–8·4	7·3–8·3	0·3
Cresol red	7·2–8·8	7·6–8·8	—
Phenolphthalein	8·3–10·0	8·1–9·0	0·9 to 0·4
Thymol blue	8·0–9·6	8 2–9·2	0·0
Thymol-phthalein	9·3–10·5	8·7–9·5	—
Nitramine	11·0–12·5	9·0–10·5	1·45

It is necessary therefore to employ buffer solutions whose hydrogen-ion concentrations are accurately known at the temperature at which the determinations are to be made, and if the measurements are to be carried out without the aid of reference solutions, then the constant of the indicator at the desired temperature must be known.

Effect of Alcohol.

Very little systematic work seems to have been done on the effect which alcohol may have on the behaviour of indicators, in spite of the fact that volumetric estimations are sometimes made in alcoholic solutions. It has a very pronounced effect on the sensitivity on certain indicators. Thus if an aqueous solution containing phenol-phthalein be rendered sufficiently alkaline to produce a slight reddening of the indicator, it will be found on the addition of alcohol that the colour becomes paler and paler and eventually disappears. Here the alcohol makes the phenol-phthalein more resistant to colour change, *i.e.*, it reduces its sensitivity, and considerably more alkali must be added to restore to the solution its original faint red coloration. If the colour is due to the existence of indicator-anions, In′, in the solution through the formation of the sodium salt, then it will be inferred that the alcohol represses the ionisation of the phenol-phthalein, *i.e.*, increases pK_{HIn}, such that much of the added alkali fails to interact and thus the free alkali raised the pH of the alcohol-water solution before the colour change becomes apparent. Kolthoff (*Rec. trav. chim.*, 1923, **42**, 251) has investigated, in a preliminary way, the effect of alcohol on many indicators in a complete range of alcohol-water mixtures. He found that nitramine, bromophenol blue, thymol blue (acid range) and curcumine became more susceptible to colour change in the presence of alcohol, whereas thymol-phthalein, phenol-phthalein, thymol blue (alkaline range), tropæolin O, tropæolin OO, methyl orange and methyl yellow do not undergo a change in colour until considerably more reagent has been added than in aqueous solutions. For the majority of indicators tested, the error involved in pH value determinations through a proportion of alcohol less than 10 per cent. by volume is usually about 0·1 pH, though the error for greater volumes becomes considerable.

Use of Indicators in Titrations.

The remaining part of this chapter will be devoted to the part played by an indicator in volumetric analysis. We saw in Chapter X that often there corresponds to the equivalence- or end-point

of a neutralisation reaction some definite pH value, and a very small excess of the titrant may, or may not, cause a considerable pH change. The indicator should be so chosen that the pH corresponding to its most marked colour change is, or only a little above, that at which the true end-point is reached.

First Perceptible Appearance of Colour of a One-Colour Indicator—its Dependence on the Concentration and Solubility.

In carrying out a titration with a one-colour indicator, HIn, such as phenol-phthalein, or paranitrophenol, the beginning of the colour change, *i.e.*, of the appearance of colour, is a matter of some importance. In the case of a one-colour indicator, it is reasonable to suppose that when the colour just becomes visible, there must be formed in the solution a small proportion of In′-ions, whose concentration is the minimum requisite for the visible production of colour. This limiting concentration will be independent of the concentration of the indicator, and will be characteristic of the indicator itself. Let this concentration be denoted by $[In']_v$, and suppose that the hydrogen-ion concentration corresponding to the visible beginning of the colour change of an indicator whose concentration is $[HIn]_a$ is $[H^{\cdot}]_a$, and that for the indicator in concentration, $[HIn]_b$ to be $[H^{\cdot}]_b$. Then

$$[H^{\cdot}]_a = \frac{[HIn]_a}{[In']_v} \times K_{HIn},$$

and

$$[H^{\cdot}]_b = \frac{[HIn]_b}{[In']_v} \times K_{HIn}.$$

Hence

$$p\mathrm{H}_a = p\mathrm{K}_{HIn} + \log \frac{[In]_v}{[HIn]_a},$$

and

$$p\mathrm{H}_b = p\mathrm{K}_{HIn} + \log \frac{[In]_v}{[HIn]_b},$$

and therefore

$$p\mathrm{H}_a - p\mathrm{H}_b = \log \frac{[HIn]_b}{[HIn]_a}.$$

Thus, we see that the first visible appearance of colour of a one-colour indicator is directly connected with the concentration of indicator. If $[HIn]_b$ were equal to 10 times $[HIn]_a$, then would $p\mathrm{H}_a - p\mathrm{H}_b = 1$, and consequently the appearance of colour in the solution having the greater indicator concentration would occur at a lower pH value, in the special case 1 pH unit below.

We have seen on page 195 that the pH range within which an

indicator changes colour is determined by the magnitude of its
constant, either as an acid or a base.   The ranges of certain indi-
cators are curtailed through the relatively small solubilities of one
or the other forms, namely, the acid form of an acid indicator, and
the alkaline form of a basic indicator.   It will be understood from
the above considerations, that saturated solutions of two indicators,
having the same dissociation constants, but having different solu-
bilities, S_a and S_b, will on treatment with alkali become coloured
at different pH values, which will be related to one another by

$$p\mathrm{H}_a - p\mathrm{H}_b = \log \frac{S_b}{S_a}.$$

Titration Exponent.

In performing titrations the worker is concerned with the pH
value at which the more or less abrupt colour change takes place,
and not with the pH range governing the whole transition.   Bjerrum
refers to these pH values as the indicator " titration-exponents,"
and denotes them by p_T.   Some generalisations have been made
by Noyes (*J. Amer. Chem. Soc.*, 1910, **32**, 825) on the incidence
of these changes.   If a one-colour indicator be used in the mini-
mum amount, then the colour first becomes perceptible only after
the indicator, HIn, has been neutralised to the extent of 25 per
cent.   Hence

$$p\mathrm{H} = p\mathrm{K}_{\mathrm{HIn}} + \log \frac{[\mathrm{In}']}{[\mathrm{HIn}]}$$
$$\therefore \quad p_T = p\mathrm{K}_{\mathrm{HIn}} + \log \frac{25}{100 - 25}$$
$$i.e., \quad p_T = p\mathrm{K}_{\mathrm{HIn}} - 0.5 \text{ (approx.).}$$

In the case of phenol-phthalein, $p\mathrm{K}_{\mathrm{HIn}} = 9.7$, and therefore
the first observable colour would be expected at pH 9.2.   It should
not be forgotten, however, that the actual value of p_T is largely
determined by the concentration of indicator employed, so much
so that if the solution had been saturated with phenol-phthalein
it would have begun to redden at pH 8.4.   On the contrary, the
very small solubility of thymol-phthalein fixes its titration exponent
at pH 9.5.

The location of the titration exponent of a two-colour indicator
is a question of greater difficulty, created by the fact that usually
one of the two colours is considerably more intense than the other,
and also that the eye may be more sensitive to one than to the
other.   Hence in following the change in colour of an indicator
during a titration, if it should happen that the first colour is more

intense than the second, the first variation in colour produced by the formation of some of the second coloured form will be somewhat delayed than would have been the case if the two colours were either equally intense, or the second the more intense. Conversely if the titration be carried out in the reverse direction the greater depth of the one colour will cause the visible change to appear at an earlier stage in the neutralisation of the indicator. Noyes found that as a rule from 5 to 20 per cent. of the indicator must be neutralised when carrying out a titration in one way, whereas when performing the titration in the opposite way the decomposition of the indicator salt must proceed to somewhere between 5 and 20 per cent., *i.e.*, corresponding to neutralisation of the indicator ranging from 95 to 80 per cent. respectively. Due to the greater intensity of the red form of methyl orange, he found that in the titration of an acid with an alkali the colour-change appeared between 20 and 30 per cent. neutralisation of the indicator. Titrating in the opposite way the change in colour became evident when between 5 and 20 per cent. of the indicator had been reacted upon.

One point of importance in the use of indicators in titrations is that their colour-changes may often be made sharper, if these changes can be confined to as little a range of pH as possible. A

TABLE 70.

INDICATOR " TITRATION EXPONENTS."

Indicator.	p_T.	Colour.	Add to 100 c.c. Solution.	
			No. of c.c.	Conc. Indicator.
				Per Cent.
Thymol blue	2·6	Yellowish-rose	1·0	1
Tropæolin OO	2·8	Yellowish-orange	1·0	1
Bromothymol blue	4	Purplish-green	0·5–1·0	1
Methyl yellow	4·(2)	Yellowish-orange	0·2–0·5	1
Methyl orange	4·(3)	Orange	0·2–0·5	1
Methyl red	5	Yellowish-red	0·2–0·5	2
Bromocresol purple	6	Purplish-green	0·5–1·0	1
Bromothymol blue	6·8	Green	0·5–1·0	1
Phenol red	7·5	Rose-red	0·5–1·0	1
Neutral red	7	Orange-red	0·2–0·8	1
Cresol red	8	Red	0·5–1·0	1
Thymol blue	8·8	Blue-violet	0·5–1·0	1
Phenol-phthalein	8	Pale-rose	0·8–1·0	1
,, ,,	9	Pale-rose	0·3–0·4	1
Thymol-phthalein	10	Pale-blue	0·5–1·0	1
Nitramine	11·6	Orange-brown	0·5–1·0	1

step towards this end may be made by using the smallest possible amounts of indicator solution. The indicators should preferably be synthetic, as those derived from vegetable sources comprise in some cases mixtures of acids and yield variations in colour extending over a wide pH range, e.g., litmus, pH 4·8-8·0. Table 70 gives the titration exponents and concentrations of commonly used indicators. It was taken from Kolthoff's *Indicators*, page 109.

Detection of End-Points by (a) Spectroscope, (b) Photo-electric Cell.

The location of the end-points of titrations of coloured solutions to which indicators were added has been investigated by Bruère (*Bull. Soc. Chim. biol.*, 1928, **10,** 283) by following the variation in the absorption spectra with the spectroscope. The indicators belonged to the phthalein and sulphone-phthalein groups, and it was found that accurate results could be obtained.

An automatic method of titration based on the variation in the intensity of light transmitted through a solution containing indicator in the vicinity of the colour-change has recently been described by Müller and Partridge (*J. Ind. Eng. Chem.*, 1928, **20,** 423). Light passes through the titration cell on to a photoelectric cell, and the variation in the intensity of light during the titration is sufficient to actuate the photoelectric cell. The current so generated is amplified by passing through a valve, when it is made to operate a relay which controls the volume of titrant run in from a burette. The method is stated to be capable of much greater precision than by the visual detection of the indicator colour-change, and this claim is substantiated by the *plate current—colour-change* curves. The whole procedure is entirely automatic and rapid which should make it of importance in routine analysis.

Titration Error of Indicators.

The fact that an indicator behaves either as an acid or a base is often overlooked as regards the error which this factor may introduce into a volumetric estimation. The following figures show that the errors involved may indeed be quite considerable. Two drops (= 0·1 c.c.) of a 1 per cent. solution of phenol-phthalein requires 0·06 c.c. of N/10-alkali ; 0·1 c.c. of 1 per cent. methyl orange ; 0·03 c.c. N/10-titrant ; 0·1 c.c. of 1 per cent. methyl red ; 0·03 c.c. N/10-titrant.

<div align="center">

CHAPTER XIV.

</div>

Most of the indicators can now be procured commercially. No attempt will therefore be made here to deal with their preparation in anything like an exhaustive manner. Nevertheless, it is thought that it might be of service to some readers if a few practical details of the methods of preparation of certain indicators and, especially, of some of the newer ones be included.

Methyl Orange.

Method I.—Dimethylaniline is allowed to react on diazo-benzene sulphonic acid in a hydrochloric acid solution.

Method II.—From aniline and dimethylaniline. Approximately equimolecular quantities of these compounds are added to an equal weight of concentrated hydrochloric-acid solution and the resulting mixture dissolved in about 15 times its weight of water. Diazotise by slowly adding $NaNO_2$, in an amount equal to one-third of the weight of HCl used, and an amount of NaOH equal to one-half of the $NaNO_2$, both dissolved in about 5 times their total weight of water. Dissolve the precipitate in HCl, reprecipitate with NaOH, wash and crystallise from hot alcohol. Sulphonate by dissolving in an excess of concentrated H_2SO_4. Pour into water and dissolve in alkali. Recrystallise from hot water.

Methyl Red.

Diazotise a well-stirred solution, composed of 20 grams of anthranilic acid, 60 c.c. of concentrated HCl and 600 c.c. of water, with a solution of 10 grams of $NaNO_2$ in 50 c.c. of water. Stand for half an hour, if no HNO_2 remains transfer to a solution of 19 grams of dimethylaniline in 20 c.c. of concentrated HCl and 20 c.c. of water. Stir for half an hour and then add 200 grams of sodium acetate. Raise carefully to 40° C. and maintain there for three hours. Stand for 24 hours at room temperature. Filter. Wash. To purify, dissolve in 100 c.c. of a 5 per cent NaOH solution at 70° C. Carefully add a boiling solution of hydrochloric acid (90 c.c. concentrated HCl + 270 c.c. of water). On

cooling, the hydrochloride of methyl red separates out as steely blue crystals.   Wash with 100 c.c. of 10 per cent. HCl.   Dry.

Yield : 28 grams.

To prepare water-soluble methyl red, dissolve the above crystals in 100 c.c. of 5 per cent. NaOH solution.   Cool and salt out with 5 grams of NaCl.   Wash.   Dry below 40° C.

Yield : 28 grams.

Neutral Red.

Dissolve 1 gram-mol. of *m*-toluylene diamine in $2\frac{1}{2}$ litres of water at 30° C.   Add paste of 1 gram-mol. of nitrosodimethyl-aniline hydrochloride and 500 c.c. of water.   Stir for 1 hour. Stand 18 hours.   Add 7 litres of water, boil and blow air through for half an hour and then add 1 gram-mol. HCl.   Salt out. Purify by making 5 per cent. solution in water, and precipitating with 10 per cent. HCl.

Phenol-phthalein.

Heat at 120° for several hours a mixture of phenol, phthalic anhydride and concentrated H_2SO_4 in the respective proportion by weight of 10 : 5 : 4.   Wash with water, dissolve in dilute alkali. Reprecipitate with acid, wash, and dry.   Purify by crystallisation from alcohol, after treatment with charcoal, and diluting with little water.   White crystals.   Melting-point, 250° C.

α-Naphthol-phthalein.

Grind 28 grams of α-naphthol to a fine powder and mix in a mortar with 15·2 grams of phthalic anhydride.   Place in an enamelled iron digester with 3 c.c. of concentrated H_2SO_4, then heat on water-bath with constant stirring at 60° C. for 4 hours, taking care that the temperature does not rise above 65° C.   Wash by decantation with water until acid free.   Treat with 4 litres of $\frac{1}{2}$ per cent. NaOH solution at 70° C.   Filter off the blue product. Cool.   Neutralise about a half of the alkali with HCl, and the remainder by passing carbon dioxide.   Brown solid remains. To purify, dissolve in NaOH and reprecipitate as above.   Yield : 7 grams.

Thymol-phthalein.

Heat a mixture of equivalent weights of thymol and phthalic acid to about 150° C.   When action ceases, cool, wash with dilute

HCl, then with water and afterwards with petroleum spirit. Recrystallise from ether-alcohol. Melting-point : 253° C.

Sulphone-phthaleins.

To prepare sulphone-phthalein indicators of the type of phenol red, a very convenient starting material is *o*-sulphobenzoic anhydride. It may be prepared from dithiosalicylic acid which is now on the market, or from anthranilic acid by the sulphydrate Sandmeyer reaction. The potassium salt of ortho-sulpho-benzoic acid may be prepared as follows : stir 300 c.c. of 65° Tw. nitric acid in a 5 litre vessel with 1·2 litres of water. Heat to about 70° C. on a steam-bath and slowly add 1 53 grams of dithiosalicylic acid (frothing !). Add 40 c.c. of nitric acid, evaporate to small bulk, and then with stirring to dryness in an enamelled iron dish on a steam-bath. Dissolve in 250 c.c. of hot water and filter. Treat filtrate whilst boiling with 90 grams of KCl. Cool and the potassium salt separates which is dried in a steam oven. The amount so obtained is about 171 grams, and this is now converted into the anhydride by the action of thionyl chloride (137 c.c.) under a reflux condenser on a steam-bath for 3 hours. After distilling off the excess of thionyl chloride under reduced pressure, the anhydride is extracted by refluxing with 300 c.c. of dry benzene. Filter and set to crystallise. Dry crystals in a steam oven. Re-extract residue with mother-liquor. Yield : 98 grams.

Phenol Red.

Melt 22·4 grams of phenol and add 20 grams of finely divided *o*-sulphobenzoic anhydride, with stirring, at 120° C. in an oil-bath. Heat for 2 hours at 120° to 125° C. and then for 8 hours at 135° to 140° C. Cool. Boil with water to extract any uncombined phenol. Dissolve residue in 11 c.c. of 30 per cent. NaOH at 60°, cool, precipitate with 12 c.c. of concentrated HCl, filter and wash. Yield : 20 grams.

Ortho-Cresol Red.

Heat 6·5 grams of *o*-cresol at 120° to 125° C., add 5 grams of *o*-sulphobenzoic anhydride and continue heating with stirring for 2 hours and finally at 135° to 140° C. for 8 hours. Extract cooled mass with *ca.* 50 c.c. of dilute NaOH, acidify with *ca.* 50 c.c. of HCl and boil to drive off excess of cresol. Dissolve solid in dilute NaOH at 60° to 70° C. Filter. Cool, pour into dilute HCl with agitation. Filter off precipitated *o*-cresol red, wash and dry. Yield : 7 grams.

Bromocresol Purple.

Dissolve 5 grams *o*-cresol red in 50 c.c. of glacial acetic acid. Heat to boiling under reflux, then add 2 c.c. of bromine in 20 c.c. of glacial acetic acid and gently boil for 1 hour.   Cool.   Filter off the bromocresol purple, wash with a little acetic acid and dry. Yield : 4 grams.

Thymol Blue.

Heat and stir a mixture of 38 grams of thymol and 25 grams of *o*-sulphobenzoic anhydride in a salt-bath at 105° C. for 12 hours. Cool, add 50 c.c. of water and heat on a water-bath.   Pour the tarry liquid thus formed into 400 c.c. of water and add 12 grams of sodium carbonate.   Extract oily matter with benzene.   Dilute clear solution to 700 c.c., filter, precipitate with dilute HCl.   Purify by redissolving in NaOH and reprecipitating with acid.   Yield : 18 grams.

Bromothymol Blue.

Dissolve 5 grams of thymol blue in 30 c.c. of glacial acetic acid.   Raise to boiling, add 2 c.c. of bromine in 10 c.c. of acetic acid and boil gently for half an hour.   Evaporate to dryness on a water-bath and recrystallise from alcohol.   Yield : 6 grams.

Bromophenol Blue.

Shake up 18 grams of phenol red with 90 c.c. of glacial acetic acid and after adding a solution of 10 c.c. of bromine in 40 c.c. of glacial acetic acid, heat on a steam-bath for $1\frac{1}{2}$ hours.   Cool.   Filter off bromophenol blue crystals, wash with dilute acetic acid and dry. Yield : 27 grams.

CHAPTER XV.

THE FUNDAMENTAL IMPORTANCE OF HYDROGEN-ION CONCENTRATIONS IN INORGANIC CHEMISTRY. THE PRECIPITATION OF HYDROXIDES.

HAVING shown how the hydrogen-ion concentrations set up during the neutralisation of an acid with either a strong base or a weak base, provided that the base is soluble in water, depends upon the dissociation constants of the reactants, we shall now proceed to consider the reactions involving inorganic bases which are insoluble in water. If it were possible to determine the affinity constants of such insoluble bases, then, together with a knowledge of their respective solubility products, it would be possible to place their reactions on a mathematical basis so far as hydrogen-ion concentrations were concerned. Nothing, however, of any real value is known of the dissociation constants of insoluble bases, neither can they be calculated with any satisfaction from the hydrolysis constants of their salt solutions by means of the formulæ derived on page 168, for unlike the equilibria there involved these reactions are often heterogeneous as the hydrolysed acid tends to cause the separation of the insoluble base, and though such a separation may not be visible there is every possibility of the base being colloidally dispersed. It is therefore necessary to choose some property which is susceptible to accurate measurement by which the bases can be compared and classified. Measurements of the basic strength by determinations of electromotive force, of heats of formation of oxides and salts, of dissociation pressures of sulphates at different temperatures, and of the hydrolysis of various salts in solution have led to different arrangements. The arrangement in the order of the dissociation constants of the hydroxides as calculated from hydrolysis data is not altogether satisfactory, for in the majority of cases sufficiently accurate measurements cannot be made.

Curiously enough, the order of the precipitation of the hydroxides by the gradual addition of alkali has until recently received no serious attention, except with regard to the separation of the rare-earths. Hildebrand's work (*J. Amer. Chem. Soc.*, 1913, **35**, 847) in this connexion was repeated and extended by the present author (*J. Chem. Soc.*, 1925, **127**, 2110-2159). A definite hydrogen-ion concentration, within narrow limits, for those salt concentrations

normally employed in analytical procedures has to be attained be-
fore the precipitation of any particular hydroxide can take place.
This would be expected from a consideration of the " solubility
product." An insoluble hydroxide, MOH, attains equilibrium
with undissociated molecules and ions in solution, thus :

$$\text{MOH (solid)} \rightleftharpoons \text{MOH (undissociated)} \rightleftharpoons M^{\cdot} + OH'.$$

The " solubility product " $= [M^{\cdot}][OH'] = [M^{\cdot}]K_w/[H^{\cdot}]$, where
$K_w = [H^{\cdot}][OH']$. The precipitation of the hydroxide thus de-
pends on the concentration of both the metal- and the hydrogen-
ions. In ordinary analytical operations, the concentrations of the
metal-ions do not vary to any considerable extent and consequently
precipitation depends largely on the hydrion concentration. The
hydrion concentrations necessary for the precipitation of a large
number of hydroxides, which have now been determined, consti-
tute a suitable basis for the classification of the hydroxides. The
order is " parallel " with the increasing magnitude of the solubility
products, but whether it is that of the basic strengths cannot be
stated with certainty ; this can be so only if the concentration of
undissociated molecules is the same for each hydroxide—a point
about which nothing is known.

Effect of Concentration, Anion, and Precipitant on the Hydrogen-Ion Concentrations required for the Pre-cipitation of Hydroxides.

Hildebrand's curves showing the pH changes during the pre-
cipitation of neodymium hydroxide from nitrate and chloride
solution, however, seemed to show that the acid radical had some
specific influence in determining the pH at which the hydroxide
began to separate, for, in the case of neodymia, the precipitation
pH from the chloride solution lay between 7 and 8, whereas it
was as low as 5 from the nitrate solution. The latter has since
been shown to be erroneous, and was undoubtedly due to the
reduction of the nitrate taking place at the surface of the electrode
by the hydrogen. The work of the author has confirmed the view
that the precipitation pH of a metallic hydroxide is independent
of the acid radical. It should be stated, however, that certain acid
radicals, particularly the chloride and nitrate, tend to delay some-
what the actual precipitation through the formation of colloidal
solutions composed of basic salts. Table 71 gives the pH values
at which thorium hydroxide began to be precipitated by N/10-
sodium hydroxide at 15° from solutions of thorium nitrate ranging
in concentration from M./1000 to M./100.

<div align="center">TABLE 71.</div>

<div align="center">EFFECT OF CONCENTRATION ON PRECIPITATION pH OF THORIUM HYDROXIDE.</div>

Concentration.	E.M.F. of H_2 Electrode against Normal Calomel.	pH.
0·001 M.	0·489	3·60
0·002 M.	0·488	3·58
0·01 M.	0·487	3·57

The difference in pH is thus very small and this range of concentrations covers those usually employed in analytical work. The differences in the pH values of precipitation from solutions of different salt concentrations are usually greater than with thorium hydroxide. The reason undoubtedly lies in the quadrivalency of thorium, for any small variation in the Th····-ion concentration of a solution will theoretically impose a quarter of that variation on the hydroxyl-ion concentration to maintain the constancy of the solubility product, [Th····][OH′]⁴. With a divalent metallic base, e.g., $Cu(OH)_2$, a change in [Cu··] of a salt solution will necessitate a change in [OH′] equal to one-half of the metal-ion change in order that precipitation may ensue. As we shall see later, metallic hydroxides are scarcely ever precipitated as such, but only in conjunction with some undecomposed salt in the form of a basic salt. Nevertheless, the dominating influence on the hydrogen-ion concentration is the precipitation of the hydroxide, for as Table 74 shows the pH values at which precipitation begins permit of the approximate calculation of solubility products of hydroxides. Fig. 59 gives some precipitation curves of copper basic sulphate from copper sulphate solutions of different concentrations with alkali, which were obtained with the quinhydrone electrode at 18° C. by Mrs. B. Westmoreland-White, B.Sc., to whom the author is indebted. Curve A refers to the precipitation from 20 c.c. of 1 M.-$CuSO_4$ with N-KOH, curve B to precipitation from 100 c.c. of 0·02 M.-$CuSO_4$ with 0·1 N-NaOH, and C to precipitation from 100 c.c. of 0·002 M.-$CuSO_4$ with 0·01 N-NaOH. The portions of the curves which occur after the initial inflexions and which show that only small changes in pH were produced as the alkali was added correspond to the hydrogen-ion concentrations prevailing during precipitation. Curves C and B lie between pH 5 and 6, with a difference of 0·4 pH value between them. Curve A indicates that precipitation from a one-molar solution took place slightly above pH 4,

showing how large may be the effect of concentration of a salt solution. For analytical work, however, such a concentration would be too great, it being preferable to employ solutions more dilute than one-tenth molar, and thereby to confine the precipitation pH values to within as narrow a range as possible. If one takes $[Cu^{..}][OH']^2$ to be 10^{-20} (Britton, *J. Chem. Soc.*, 1925, **127**, 2799) and substitutes for $[Cu^{..}]$, the concentrations employed above as rough estimates of their respective $Cu^{..}$-ion concentrations, it is found that the pH at which a precipitate separates from 1 M.-CuSO$_4$ solution is pH 4·1, from a 0·02 M.-solution at pH 5, and from a 0·002 M.-solution at pH 5·5. These values are in good accord with the values shown

by the curves. A pH value of 5·4 was found by the author using the oxygen electrode for precipitation from a solution whose CuSO$_4$ concentration, after the free acid had been neutralised, lay between those used for curves B and C. Curve A$_H$ is interesting in that it refers to the precipitation reaction between 20 c.c. of M.-CuSO$_4$ and N-KOH and was obtained by the glass electrode by Hughes (see p. 88). The pH values were extrapolated from his data. The proximity of the quinhydrone curve, A, with A$_H$ shows the glass

FIG. 59.—Precipitation with Alkali from Copper Sulphate Solutions.

electrode is satisfactory. Moreover, it is probable that the small differences indicated are attributable to the manner in which the precipitation was carried out as regards stirring. The curves also show that precipitation was complete when 30 c.c. of alkali were added instead of the theoretical amount, *viz.*, 40 c.c., through the separation of a precipitate having the composition 4CuO,SO$_3$,xH$_2$O (see p. 276). Considerably more work is desirable on the effect on concentration on the precipitation pH's. The author avoided differences arising from such a source by always employing solutions of approximately the same concentration in his various comparative studies.

The effect of the anion and of the basic nature of the precipi-

tant is shown in Fig. 60 in connexion with various thorium salt solutions. Precipitation began at the same pH in every case.

Curves 1, 2, and 3 represent the titrations of 100 c.c. of M./100-solutions of thorium nitrate, chloride, and sulphate respectively, with 0·1016 N-sodium hydroxide, and curve 4 that of 100 c.c. of M./100-thorium nitrate with 0·1115 N-ammonium hydroxide, at 15°. The commencement of precipitation, *i.e.*, the first appearance of turbidity, is shown by arrows. As a rule, the E.M.F's were steady (in some cases an hour elapsed before the next reading was taken), but they were not always so in those stages of the titration which indicated the rapid changes in hydrion concentration, the end of the precipitation occurring. The last section
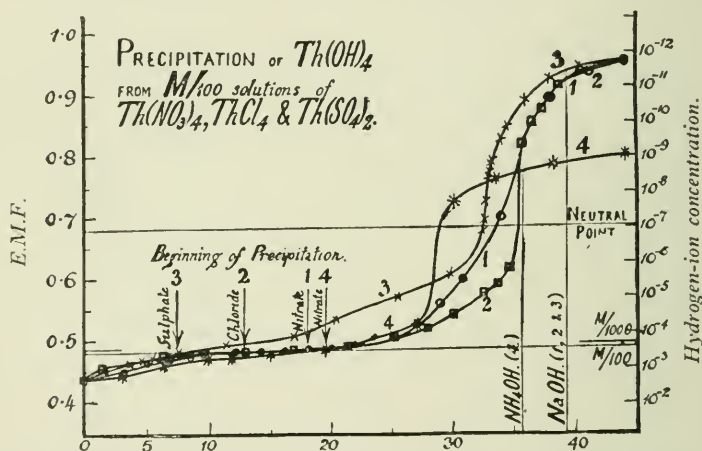
Fig. 60.—Precipitations from Thorium Salt Solutions with Alkalis, followed by the Hydrogen Electrode, compared with the Normal Calomel Electrode.

of curve 1 represents a gradual diminution in hydrion concentration and the readings were stationary during the intervals (5 to 15 minutes) allowed for the attainment of equilibrium. Curve 2, chloride, shows a sudden yet well-defined change, but in the case of the thorium sulphate titration (curve 3) the change was irregular and long periods were necessary before constant readings were obtained. Appreciable amounts of alkali had to be added before the commencement of precipitation, and thereafter, in the case of the nitrate and the chloride solutions, there was a distinct tendency for a constant pH to be maintained during the addition of the greater portion of the alkali. It is probable that this corresponds to the separation of a precipitate of uniform composition.

In neither case was thorium hydroxide precipitated as such.

Fig. 60 shows that precipitation was complete and the mother-liquors had become alkaline some time before the stoichiometrical quantities of alkali had been added. The following table gives the amounts of alkali which were added before precipitation ensued and the amounts of alkali which had to be added before the solutions became neutral (pH 7).

TABLE 72.

EFFECT OF ANION AND PRECIPITANT ON THE PRECIPITATION OF THORIA.

Curve.	Solution and Precipitant.	Precipitation began		Equivs. of Alkali required for Neutrality.	Composition of Precipitate.
		pH.	Equivs. of Alkali.		
1	$Th(NO_3)_4$ and NaOH	3.57	1.85	3.43	$Th(OH)_{3.43}(NO_3)_{0.57}$
2	$ThCl_4$ and NaOH	3.51	1.30	3.58	$Th(OH)_{3.58}Cl_{0.42}$
3	$Th(SO_4)_2$ and NaOH	3.53	0.78	3.31	$Th(OH)_{3.31}(SO_4)_{0.35}$
4	$Th(NO_3)_4$ and NH_4OH	3.57	2.21	3.24	$Th(OH)_{3.24}(NO_3)_{0.76}$

The last two columns of the above table show that the precipitate formed in each titration was basic, being somewhat less so when the precipitant was ammonium hydroxide. The protracted inflexions produced during the last stages of precipitation show that the precipitates at first formed were less basic and suffered some decomposition on further addition of alkali. This seems to have taken place readily in the cases of the nitrate and the chloride, but the slowness with which apparent equilibrium was attained in the second part of the sulphate titration indicates that the basic sulphate was undergoing hydrolysis with much greater difficulty. It seems almost unnecessary to say that the amounts of acid radical retained by these precipitates were too great to be accounted for by adsorption from such dilute solutions. These precipitates were not completely decomposed even when excess of alkali was added. It is also an interesting fact that the sulphate radical tends to hold more tenaciously to form stable basic salts than do other acid radicals, and this is true of the basic micelles present in solutions like zirconium sulphate solutions and so exercise a peculiar effect on their chemical properties (see p. 270).

Another remarkable fact arising from these titrations is that alkali ranging in amounts from 0.78 to 2.21 equivalents to one molecule of thorium salt had to be added before the appearance of a precipitate. These amounts, which vary with the nature of the anion and the precipitant, do not permit of a guess as to the way in which the thorium hydroxide, or basic complex, is held in solution until the attainment of the pH requisite for precipitation. According to Ordway (*Amer. J. Sci.*, 1858, **26**, 197), Berzelius

observed that when alkali was added to a thorium sulphate solution precipitation was delayed owing to the formation of what appeared to be *un soussel soluble*. Ordway directed attention to several other examples of " soluble basic salt " formation. It will be shown in the course of the following chapters that these so-called soluble basic salts exert a pronounced influence on some of the reactions of the metals of which they are characteristic. It is surprising that " soluble basic salts" are generally formed by those metals the valencies of which are greater than two, although this is the case neither with the tervalent rare-earths nor with bivalent
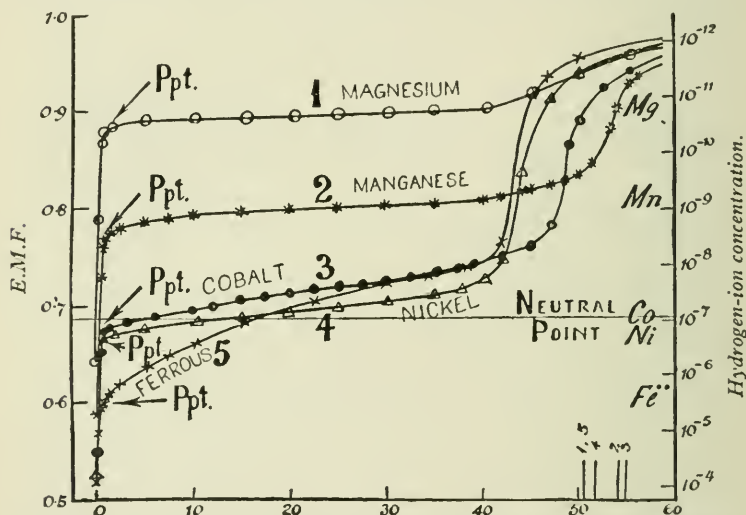
FIG. 61.—Precipitations followed by the Hydrogen Electrode (against the Normal Calomel Electrode).

beryllium, which has a remarkable property of forming these basic solutions.

The Precipitation of the Hydroxides of Magnesium, Manganese, Cobalt, Nickel, and Ferrous Iron.—The following table gives particulars of the solutions used in typical titrations, together with the amount of alkali required to cause incipient precipitation. The courses of the titrations are shown in Fig. 61.

In contrast with the thorium salt titrations, the first few drops of sodium hydroxide caused a rapid diminution in hydrion concentration until a value was obtained at which precipitation commenced. Thereafter, precipitation proceeded with very little change in pH until the separation was nearly complete. The titration of ferrous sulphate solutions was a matter of some difficulty.

Table 73.

Precipitation of Hydroxides (Fig. 61).

Titration and Curve No.	Solution Titrated. 100 c.c.	Normality of NaOH.	C.c. of NaOH theoretically required.	Precipitation first began.		Precipitation ended. Equivs. NaOH.
				pH.	C.c. of NaOH.	
1	0·025 M.-MgSO$_4$	0·0990	50·5	10·49	1·6	1·64
2	0·024 M.-MnCl$_2$	0·0900	54·0	8·41	1·0	1·93
3	0·0247 M.-CoCl$_2$	0·0900	54·8	6·81	0·9	1·75
4	0·025 M.-NiCl$_2$	0·0967	51·7	6·66	0·6	1·66
5	0·025 M.-FeSO$_4$	0·0990	50·5	5·49	0·8	1·71

As is well known, manganous and ferrous hydroxides on exposure to air readily become oxidised, and consequently the titrations involving their precipitation were performed in vessels which were stoppered as far as possible. Even so, it was not possible to prevent some oxidation from taking place, although plenty of hydrogen was passing through the solutions. The curves, however, were reproducible, and there is little doubt that the voltage readings indicated correctly the changes in hydrion concentration, for the pH data agreed with those found colorimetrically.

Precipitation was again complete in each case some time before the theoretical amount of alkali had been added. Curve No. 1, magnesium sulphate, shows that the final inflexion began when 1·64 equivalents of sodium hydroxide had been added. The gradual slope of the inflexion was evidently due to the partial decomposition of the basic sulphate, originally precipitated. A similar inflexion, but steeper, took place in magnesium chloride titrations. Hildebrand and Harned (*Orig. Com. 8th Inter. Cong. Appl. Chem.*, 1912, **1**, 217) and Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35,** 847) have also studied by means of the hydrogen electrode the precipitation of magnesium hydroxide and have suggested that the electrometric titration of hydrochloric acid solutions of dolomite might be used for the estimation of the magnesia with an accuracy of about 1 per cent., despite the fact that the values obtained by them showed a variation of 5 per cent. The difficulty is that magnesium hydroxide is not precipitated simply from either chloride or sulphate solutions to give sharp inflexions, but indefinite basic precipitates are formed which give poorly defined inflexions ; this renders it impossible to assign a point on the curve which exactly corresponds to the neutralisation of all the acid which was originally combined with the magnesium hydroxide. According to Kolthoff (*Rec. trav. chim.*, 1922, **41,** 787), Pinkof (*Thesis*, Amsterdam, 1919, p. 34) has investigated the electrometric estimation of magnesia by means of the Hg|HgO|Alkali electrode, but obtained unsatisfactory inflexions, even when an excess of alkali

was added and the free alkali afterwards titrated. Kolthoff recommended shaking the magnesium salt solution with an excess of alkali and allowing to stand so as to render the decomposition of the basic salts as complete as possible before titration.

Calculation of Solubility Products.

Although basic precipitates were always produced, it is possible to calculate from the curves the values of the solubility products of the hydroxides, which are in good agreement with those obtained by other methods. As a rule, precipitation began somewhere near the point of the first inflexion, although often at a pH which was a little less than that at which the main precipitation took place. This was probably due to the precipitate having been formed at a point in the solution where the precipitation value of pH had been temporarily exceeded, and time not having been allowed for its re-solution. If, therefore, the two straight portions of the curve be produced, it is probable that the point of intersection corresponds more nearly to the amount of alkali which had to be added to produce incipient precipitation, and also to the actual hydrion concentration at which precipitation under ideal conditions would have commenced. This point represents the limiting conditions necessary to form a precipitate. The concentration of metal-ions can be calculated from the amount of alkali, and K_w at 18° being 0.73×10^{-14}, the concentration of hydroxyl-ions can be found. Columns 2 and 5 in the following table give the co-ordinates of these points for the curves shown in Fig. 61.

TABLE 74.

SOLUBILITY PRODUCTS CALCULATED FROM CURVES IN FIG. 61.

No.	E.M.F.	pH.	pOH.	C.c. of NaOH.	$C_M^{..} \times 10^4$.	$[\text{Me}^{..}][\text{OH}']^2$.
1	0·892	10·61	3·52	0·5	2·5	$2·3 \times 10^{-11} = [\text{Mg}^{..}][\text{OH}']^2$
2	0·794	8·85	5·27	1·0	4·5	$1·3 \times 10^{-14} = [\text{Mn}^{..}][\text{OH}']^2$
3	0·680	6·92	7·22	1·0	4·5	$1·6 \times 10^{-18} = [\text{Co}^{..}][\text{OH}']^2$
4	0·675	6·81	7·32	0·8	3·9	$8·7 \times 10^{-19} = [\text{Ni}^{..}][\text{OH}']^2$
5	0·615	5·77	8·37	0·6	3·0	$4·5 \times 10^{-21} = [\text{Fe}^{..}][\text{OH}']^2$

The method is, of course, open to the objections (a) the difficulty of estimating accurately the amount of alkali required, and (b) the fact that basic salts were actually precipitated which may have had some effect on both the hydroxyl- and the metal-ion

concentrations.   Nevertheless, the values of the solubility products are generally in good agreement with those recorded in the literature.

Use of Ammonium Chloride in Analysis.

These curves throw considerable light on the function of ammonium salts in preventing the precipitation of certain hydroxides. The addition of ammonium salts to ammonia may be such that the pH is depressed below the precipitation value of either magnesium or manganous hydroxide.   The approximate hydrogen-ion concentration of a solution containing ammonium hydroxide and ammonium chloride is given by

$$[H^{\cdot}] = \frac{[NH_4Cl]K_w}{[NH_4OH]K_{NH_4OH}},$$

where $K_w = 10^{-14.14}$ and $K_{NH_4OH} = 10^{-4.64}$ at $18°$.

If ammonium chloride is regarded as being completely dissociated, the minimum number of molecules of ammonium chloride to be added to each molecule of ammonia to increase the hydrion concentration to that required just to start precipitation of (a) magnesium hydroxide is 0·08, (b) manganous hydroxide, 4·5, (c) cobaltous hydroxide, 380, and (d) hydroxides of nickel and ferrous iron, still more.   In analytical processes, the condition for the prevention of the precipitation of the hydroxides of magnesium and manganese is easily satisfied, but the sole cause of the partial or non-precipitation of the other hydroxides is the magnitude of the quantities of ammonium chloride that must be added.   Herz (Z. anorg. Chem., 1900, **23**, 227) believed that the behaviour of ammonium chloride in depressing the hydroxyl-ion concentration was also the cause of the non-precipitation of zinc hydroxide, but, as will be shown later, zinc hydroxide is precipitated while the mother-liquor is still very slightly acid and consequently its precipitation could not be affected by the ammonium salt in the same way as in the foregoing instances.   It is more probable, as has been suggested by several investigators, that it is the ammonia itself which maintains the hydroxides of zinc, cobalt, and nickel in solution through the formation of complex ions.   No explanation, however, appears to be forthcoming to account for the small effect which ammonium chloride has on the precipitation of ferrous hydroxide.   The researches of Lovén (loc. cit.), Treadwell (Z. anorg. Chem., 1903, **37**, 326), and Herz and Muhs (ibid., 1904, **38**, 138) have all led to the conclusion, given more directly by

these titrations, regarding the influence of ammonium salts in preventing the precipitation of magnesium hydroxide. There are no grounds for attributing it to the formation of a complex magnesium anion—an explanation which is still to be found in some text-books.

The Precipitation and the so-called Amphoteric Nature of the Hydroxides of Zinc, Chromium, Beryllium, Aluminium, Bivalent Tin, and Zirconium.

Those hydroxides, including zirconium hydroxide, which are generally supposed to have both basic and acidic properties will now be considered, first with respect to their precipitation, and secondly with respect to the changes in hydrion concentration produced when they react with sodium hydroxide in various proportions. It is very doubtful whether zirconium hydroxide is amphoteric ; Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 847), however, has obtained electrometric evidence for the existence of zirconates.

Aluminium and Beryllium Hydroxides.

We shall, in the first place, consider the amphoteric nature of aluminium and beryllium hydroxides, and shall therefore direct
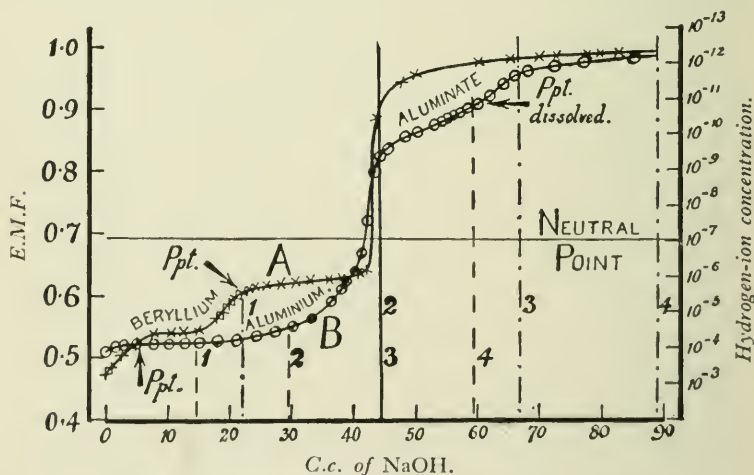
FIG. 62.—Hydrogen Electrode Precipitation Curves, showing Amphoteric Nature of Aluminium Hydroxide.

our attention to the hydrogen electrode curves given in Figs. 62 and 63 ; the particulars of the solutions titrated being given in Table 75 (Britton, *J. Chem. Soc.*, 1925, **127**, 2121 ; 1927, 422).

TABLE 75.

Solution 100 c.c. of—	Titrated with—	Precipitation began at—		Precipitate Dissolved at—	
		pH.	Equivs. Alkali per 1 Al.	pH.	Equivs. Alkali per 1 Al.
0·00667 M.-Al₂(SO₄)₃	0·090 N-NaOH	4·14	0·35	10·8	4·13
0·00349 M.-Al₂(SO₄)₃	0·0447 N-Ca(OH)₂	4·14	0·32	10·2	3·90
0·00333 M.-AlCl₃	0·0558 N-Ba(OH)₂	Opalescent 4·76	2·09	—	—
,,	,,	Coagulated 6·50	2·71	10·4	4·02
0·00408 M.-AlCl₃	0·0391 N-Sr(OH)₂	Opalescent 4·69	1·92	—	—
,,	,,	Coagulated 6·50	2·88	10·6	4·02
0·02 M.-BeSO₄	0·090 N-NaOH	5·69	1·04 (to 1 Be)	—	—

Aluminium.

The aluminium sulphate curves in Figs. 62 and 63 show that precipitates did not visibly begin to form until somewhat
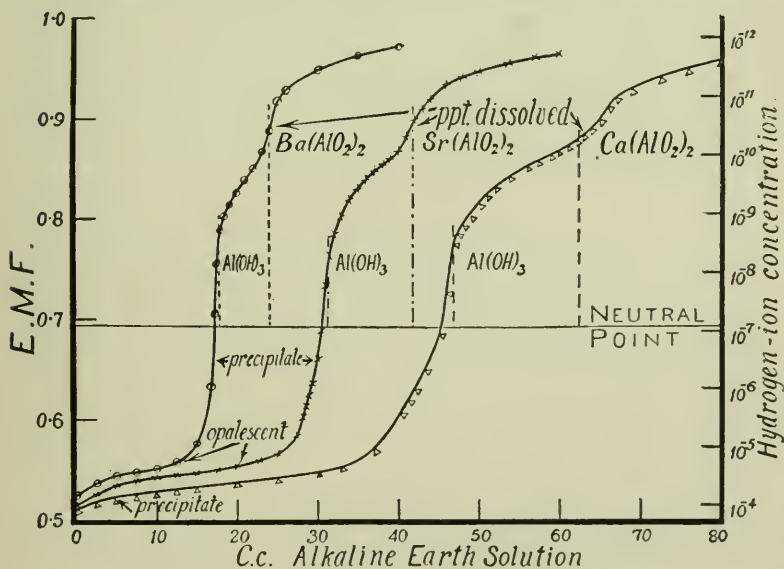
FIG. 63.—Amphoteric Nature of Aluminium Hydroxide.

over 0·3 equiv. of alkali had been added, and when the same pH

had been reached, *viz.*, *p*H 4·1. In the aluminium chloride reactions with strontia and baryta the solutions remained clear until 2·09 equiv., *p*H 4·76, and 1·92 equivs., *p*H 4·69, respectively, of alkali had been added ; opalescence only was then produced, coagulation of the precipitates not occurring until 2·71 and 2·88 equivs., respectively, had been added, and a considerably higher *p*H attained, *viz.*, 6·5. This delay in precipitation, despite the fact that the requisite precipitation *p*H 4·14, had been exceeded, and that nearly the total stoichiometrical quantity of alkali had been added, is due to the characteristic tendency of chlorides to promote the formation of colloidal solutions—the dispersed particles formed in the initial stage of the reactions being too small to affect the appearance of the solution to the unaided eye. A similar instance is that of the chloride and sulphate of zirconium (Britton, *J. Chem. Soc.*, 1925, **127,** 2125). In the case of the titration represented in Fig. 62 precipitation did not begin until the dissolved aluminium sulphate had acquired the composition $Al_2O_3,2·65SO_3$, and was complete when 2·85 equivalents had been added, thereby showing that the basic precipitate contained $Al_2O_3,0·15SO_3$. Williamson (*J. Physical Chem.*, 1923, **27,** 284) found that the precipitates formed by the addition of 1 to 2 equivalents of sodium hydroxide were of nearly constant composition and approximated to $Al_2O_3,0·6SO_3,3H_2O$. Miller (*U.S. Public Health Reports*, 1923, **38,** 1995) found that the greatest insolubility of the precipitate occurred when 2·75 equivalents of sodium hydroxide had been added and a hydrion concentration between $10^{-6·7}$ and 10^{-7} had been reached. This state corresponds to the maximum decomposition of the basic sulphate which was first precipitated.

The solutions became neutral when the sodium hydroxide and the alkaline earths had been added in amounts slightly less than those required for the formation of aluminium hydroxide owing to the retention by the precipitates of some of the acid radical present in the original salts. In each of the titrations, the precipitates redissolved completely when approximately another equivalent of alkaline earth had been added, the dissolutions being reflected in the characteristic aluminate inflexions of the titration curves extending over a *p*H range from 8 to 10·5. Magistad's (*Soil Science*, 1925, **20,** 181) results on the solubility of alumina in sodium hydroxide solutions of varying *p*H are important in that they show that the solubility first becomes perceptible at *p*H 7·55, being then 2 parts per million ; at *p*H 8·35, the solubility is 8·4 parts, but thereafter it increases rapidly to 34·6 parts per million at *p*H 8·95. Hence, it appears probable that the formulæ M^1AlO_2

and $M^{II}(AlO_2)_2$ represent the condition in which aluminium hydroxide exists in solutions of the hydroxides of the alkali- and alkaline-earth metals respectively.   In no other instance of the so-called amphoteric hydroxides is such an inflexion produced. Incidentally, in all cases the amounts of alkali required to dissolve the hydroxides, except that of zirconium, which does not dissolve, are considerably in excess of that denoted by the formulæ of the salts which have been said to be formed.   In the case of aluminium hydroxide only is the amount of alkali required for its re-solution approximately equal to that suggested by the formula $NaAlO_2$, and is also independent of the concentration of the sodium hydroxide used (compare Britton, *Analyst*, 1921, **46,** 363).   It is possible that the other hydroxides may be acidic in their behaviour towards alkalis, but to so small an extent that the hydrogen-ion concentration of the alkali solution is scarcely affected.

It should be mentioned that in the calcium hydroxide titration a fine precipitate containing both calcium and aluminium began to separate at pH 11·7 when 90 c.c. of lime water had been added. It follows, therefore, that the disappearance of alumina from " soil solutions " cannot be attributed, as Marais (*Soil Science*, 1922, **13,** 368) states, to the formation of an insoluble calcium aluminate, for the hydrogen-ion concentration of ordinary " soil solutions " never becomes so low as pH 11·7.   No precipitates were formed in the other two titrations, even although large excesses of the reactants were added.   The conditions under which the solid aluminates of barium may exist have recently been investigated by Malquori (*Gazzetta*, 1926, **56,** 54).

Beryllium.

The other curve in Fig. 62 which represents the titration of beryllium sulphate, has two distinct sections in the acid zone. Precipitation was delayed until the beginning of the second section had been reached, when 1·04 equivalents of sodium hydroxide had been added.   Thus the beryllium sulphate had to be rendered basic to the extent shown by the formula $BeSO_4,Be(OH)_2$, before a precipitate began to separate.   Although the beryllium sulphate had become so basic, the solution remained perfectly clear and betrayed no sign of colloidality.

The fact that there was a marked inflexion in the hydrion curve just at the stage when the first half of the stoichiometrical amount of sodium hydroxide had been added seems to indicate some fundamental difference between the first and second hydroxyl groups of beryllium hydroxide which gives rise to the formation

of soluble basic salts in which the first beryllium valency is attached to the weaker hydroxide group. It must be stated, however, that concentrated solutions of beryllium sulphate can be rendered still more basic to the extent of 2 mols. of $Be(OH)_2$ to 1 mol. of $BeSO_4$. It is probable, whether the basic sulphate does or does not exist in solution as a definite chemical compound, that the solution is mainly colloidal in nature, in spite of the fact that it is clear and is not coagulated by electrolytes. The colloidal aggregates of beryllium hydroxide which probably exist in some type of combination with the sulphate groups appear to be capable of ionisation, although to a less extent than would have been the case had the sulphate radicals been united with beryllium simply. If these basic solutions happen to be examples of colloidal electrolytes, it would be expected that the solution of beryllium hydroxide in a beryllium sulphate solution, being brought about by the formation of aggregates of the beryllium hydroxide and the beryllium sulphate, would be accompanied either by a diminution in the number of osmotically active particles, partly present as an ionisable colloid and partly in true solution, or, in the extreme and improbable case, by no change in number. Some support for this view is to be found in the observations of Parsons, Robinson, and Fuller (*J. Physical Chem.*, 1907, **11**, 651), who found that the effect of dissolving beryllium hydroxide in solutions of beryllium sulphate was to raise the freezing-point and to reduce the conductivity.

The beryllia on becoming completely precipitated retained sulphate and corresponded to $BeO,0\cdot045SO_3$, for 1·9 equivalents of NaOH were necessary. The alkaline branch of the beryllium sulphate curve indicates pH values which would have been produced by an excess of alkali, and this was, in spite of the re-solution of the beryllium hydroxide which was taking place. The re-solution of the beryllium hydroxide was not complete when 90 c.c. of alkali had been added, which amount was a little in excess of that required to form sodium beryllate, Na_2BeO_2, neither did the titration curve give any indication that combination had taken place. The amount of alkali requisite for re-solution varies with the concentration of the alkali used (*vide* Britton, *Analyst*, 1921, **46, 363).

Hydroxides of Zinc, Chromium, Bivalent Tin, and Zirconium.

The particulars of the titrations illustrated in Fig. 64 are given in Table 76. They were performed at 18° C. with the hydrogen electrode compared with the normal calomel electrode.

Zinc.

The curve representing the precipitation of zinc sulphate with sodium hydroxide shows that a basic sulphate was obtained. Precipitation was complete when 1·53 equivalents of alkali had
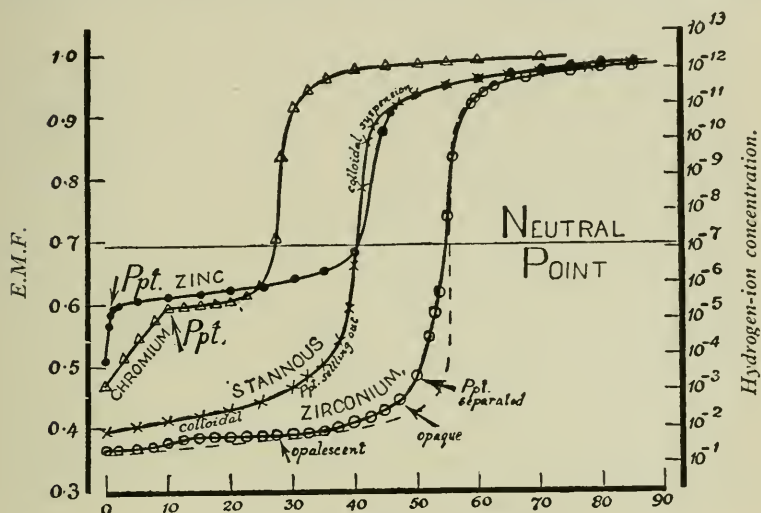
FIG. 64.—Precipitation of Hydroxides.

been added, which may have been due to the separation of a basic sulphate, $ZnSO_4,3ZnO,xH_2O$. As in other cases, the amount of alkali required was determined by the rate at which it was added,

TABLE 76.

Solution 100 c.c.	Normality of NaOH.	Precipitation Began.		Precipitation Complete.
		pH.	C.c. NaOH.	Equivs. NaOH.
0·025 M.-$ZnSO_4$	0·090	5·20	0·6	1·53
0·005 M.-$Cr_2(SO_4)_3$, K_2SO_4 (violet)	0·100	5·34	10·0	2·75
0·020 M.-$SnCl_2$	0·0932	—	—	1·86
		Opalescent at		
0·01 N-HCl and	0·090	1·86	27·5	—
		Pptd. at		
0·01 M.-$ZrCl_4$	0·090	2·79	47·5	3·75

it appearing to be a rule that the more slowly the alkali is added the less basic will be the precipitate; this, once formed, is decomposed slowly by further additions of alkali.

Complete re-solution of the zinc hydroxide did not take place in the course of the titration, although more than two molecules of sodium hydroxide were added in excess of that required to form zinc hydroxide. These measurements give no insight into the acidic nature of zinc hydroxide, for no inflexions occurred when alkali in amounts required to form the zincates having the respective formulæ $NaHZnO_2$ and Na_2ZnO_2 had been added. Calculation, however, shows that the concentration of hydroxyl-ions in the alkaline solutions was slightly less than would have been the case had no substances other than the alkali been present. For example, the pH of the solution containing the alkali required to form $NaHZnO_2$ was 12·06 as compared with the calculated value 12·25. It is probable that the diminution in hydroxyl-ion concentration was due both to some chemical action and to ad-sorption having taken place. This view is supported by the con-ductivity measurements of Chatterji and Dhar (Faraday Soc., " Symposium on Colloids," 1921, p. 123), who state that whereas the conductivity of sodium hydroxide was not appreciably changed by the addition of the majority of amphoteric hydroxides, the change when zinc hydroxide was added was pronounced. Similar observations were made by Carrara and Vespignani (*Gazzetta*, 1900, **30**, 35) with potassium hydroxide solutions of zinc hydroxide. Hildebrand and Bowers (*J. Amer. Chem. Soc.*, 1916, **38**, 785) studied with the hydrogen electrode the reaction of alkalis with certain zinc salts, and they claim to have obtained distinct evidence of the existence of monobasic zincic acid, $HHZnO_2$, for they found a sudden increase in pH at the point where the amount of sodium hydroxide added was that required for the formation of $NaHZnO_2$. Repeated titrations have been made by the author on zinc salt solutions of the concentration used by Hildebrand and Bowers, but hitherto their observation has not been confirmed. It is interesting to recall that since Hildebrand and Bowers's paper appeared Goudriaan (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **22**, 179) has investigated the isotherm at 30° of the ternary system $Na_2O-ZnO-H_2O$ and has found that the only salt of sodium and zinc hydroxides is $Na_2ZnO_2,4H_2O$, which happens to exist in equilibrium with concentrated sodium hydroxide solutions con-taining from 27·8 to 39·2 per cent. of Na_2O. This salt is decom-posed by water and so are the liquid phases with which it exists in equilibrium, for on dilution they deposit zinc hydroxide.

Chromium.

Chrome alum was used for the titration as it is the most suitable violet salt. The reader is referred to page 376 concerning differ-

ences between the violet and green forms. No precipitate was formed until one-third of the stoichiometrical amount of sodium hydroxide had been added—the pH having previously rapidly increased until the precipitation pH had been reached. The amount of alkali required to cause the beginning of precipitation seems to suggest that the basic salt retained in the solution had the formula $Cr(OH)SO_4$. It is probably a coincidence, for dissolved chromium sulphate can be rendered more basic and still remain in solution. The curve shows that the mother-liquor became alkaline when 2·75 equivalents of alkali had been added— an amount pointing to the final composition of the precipitate being $Cr_2O_3,0·25SO_3$. Williamson (*J. Physical Chem.*, 1923, **27**, 384) found, by adding varying amounts of sodium hydroxide to a decimolar solution of chrome alum, that when from 1 to 2·5 equivalents of alkali are added to one molecule of chrome alum the precipitates are almost constant in composition, $Cr_2O_3,0·7SO_3$, $3·6H_2O$, but when 3 equivalents are employed the precipitate is still more basic, as shown by the formula $Cr_2O_3,0·28SO_3,3·18H_2O$. This formula is similar to that indicated by the titration. Thus it appears that during the steady increase in pH shown when from 10 to 22 c.c. of alkali were being added, a basic sulphate of approximately constant composition was being formed, which after precipitation became more hydrolysed by the further addition of alkali.

The titration curve affords no evidence of the constitution of alkaline solutions of chromium hydroxide, although the amount of alkali which was added was in excess of that required to form Na_3CrO_3. The amount of alkali was insufficient to dissolve the chromium hydroxide. The potential differences obtained in the alkaline solutions pointed to hydroxyl-ion concentrations which were a little less than those obtained by calculation. The difference may probably be accounted for by adsorption by the chromium hydroxide or possibly by some little union having taken place. Fricke and Windhausen (*Z. anorg. Chem.*, 1924, **132**, 273) have also shown that there is a slight difference in hydroxyl-ion concentration observable between sodium hydroxide solutions and those of chromium hydroxide in sodium hydroxide of the same concentration when measured by the Hg|HgO electrode.

Stannous Tin.

The stannous chloride solution used in the titration shown in Fig. 64 was turbid and became more and more so until 30 c.c. of alkali had been added, when a heavy precipitate began to settle ;

the precipitate passed back again into colloidal suspension as soon as the solution had become alkaline ($pH = 8\cdot7$) and 41·0 c.c. of sodium hydroxide had been added. By calculating the amounts of hydrolysed hydrochloric acid from the titration pH data, it is possible to find the compositions of the basic stannous chloride aggregates at different stages in the titration. It will be found that they varied in composition from $SnCl_{1\cdot33}(OH)_{0\cdot67}$ to $SnCl_{0\cdot55}(OH)_{1\cdot45}$ during the addition of the 30 c.c. of alkali and yet remained in colloidal suspension. The molecular proportion of hydrochloric acid hydrolysed gradually became less as the titration proceeded and it was not until the particles had become basic to this extent represented by the latter formula, and the concentration of the free hydrochloric acid with which they had existed in equilibrium had become relatively small, that the colloidal solution coagulated. The solution became neutral when 40 c.c. of alkali had been added, showing that chloride was still being retained by the stannous hydroxide, its composition having then become $SnCl_{0\cdot14}(OH)_{1\cdot86}$. The fact that peptisation of the precipitate took place immediately the mother-liquor became alkaline seems to be important, and it may be that the reaction of the alkali with the retained chloride in the precipitate was largely responsible. No inflexion was produced in the curve in the alkaline zone.

Zirconium.

The precipitation of zirconia from a solution in hydrochloric acid has been investigated (Fig. 64) and also the change in pH in the mother-liquor when the precipitated zirconium hydroxide was in presence of an excess of sodium hydroxide. No inflexion was produced in the alkaline section, though one might have been expected if sodium zirconate had been formed. There appears to be absolutely no grounds for regarding zirconium hydroxide as amphoteric. Unlike the other hydroxides, that of zirconium is not dissolved by alkalis under any condition. In common with all other gelatinous hydroxides, it adsorbs salts from solutions in which it may be suspended, and on precipitation with an excess of alkali does naturally adsorb some alkali, the amount depending on the quantity of alkali present. These precipitates do not hold the alkali in any form of combination, as would be the case if they contained insoluble zirconates. It is remarkable that whilst alumina is one of the few oxides which can be considered with any degree of certainty to be amphoteric in the wet state, it should be the only one which is definitely amphoteric in the dry state, yielding on fusion with alkalis or with alkali metal carbonates products which are soluble.

The titration curve gives some insight into the mechanism of precipitation. The hydrochloric acid solution was prepared from a basic zirconium chloride which contained 1·737 mols. of Cl to 1 mol. of ZrO_2. The basic chloride dissolved in water to give a perfectly clear solution. An aqueous solution, 0·04 normal with respect to the chloride content, was hydrolysed immediately after preparation to the extent of 54 per cent. The dotted line in the diagram represents the neutralisation curve of hydrochloric acid solution having the same chloride concentration as that of the acid solution of zirconium chloride with the same alkali solution. The small but definite inflexion which occurred when 11·1 c.c. of alkali had been added is remarkable. It marks the end of the neutralisation of the excess of acid over that required to form zirconium tetra-chloride and thus points to the existence in solution of zirconium chloride, although considerably hydrolysed. This is opposed to the generally accepted view that the chloride dissolves as " zirconyl chloride," $ZrOCl_2$, dissociating into " zirconyl " ions, $ZrO^{\cdot\cdot}$, and Cl', and free hydrochloric acid. The solution began to become opalescent when 27·5 c.c. of alkali had been added, and this was before the amount of alkali had been added which was necessary to form either $ZrOCl_2$(33·3 c.c.) or the basic salt from which the solution was prepared (36·2 c.c.). As solutions of both these substances happen to be perfectly clear, it follows that the premature opalescence obtained in the titration must have been due either to the electrolytes present or to the hastened growth of the colloidal particles owing to the rate at which the alkali was added. It must have been due to the latter, for salts may be added to basic zirconium chloride solutions of similar composition without producing any perceptible effect. The zirconium chloride curve tends to approach the hydrochloric acid curve when approximately two equivalents of sodium hydroxide have been added (33·3 c.c.). At this stage the chloride radicals in combination with the zirconium were undergoing the maximum hydrolysis. The solution became increasingly colloidal in appearance as the alkali was added until it became opaque and coagulation suddenly took place (47·5 c.c.). Table 77 gives the fractions which had suffered hydrolysis of the portions of zirconium chloride which had not entered into the reaction at the various stages in the titration, from which have been found the compositions of the unhydrolysed basic zirconium chloride together with the molar proportions of the free acid which had been hydrolysed.

In these calculations it has been assumed that the hydrochloric acid was completely dissociated. The degree of hydrolysis of the zirconium chloride in the free acid solution was obtained by

subtracting the hydrion concentration produced by the excess of acid from the total hydrion concentration calculated from the observed voltage.

TABLE 77.

BASIC NATURE OF ZIRCONIUM SALT SOLUTIONS.

C.c. of NaOH.	E.M.F.	Atoms of Cl Neutra'ised.	Fraction of Unneutralised HCl Hydrolysed.	Comp. of Basic Chloride to 1 Atom of Zr.		Mo's. of HCl Hydrolysed.	Remarks.
				OH.	Cl.		
0	0·366	0	0·529	2·12	1·88	3·12	Free HCl
11·1	0·380	0	0·579	2·32	1·68	2·38	,,
22·2	0·386	1·0	0·670	3·01	0·99	2·01	Clear
27·8	0·390	1·5	0·714	3·28	0·72	1·78	Opalescent
33·3	0·393	2·0	0·828	3·66	0·34	1·66	,,
36·2	0·397	2·267	0·831	3·70	0·30	1·44	,,
38·9	0·406	2·5	0·685	3·53	0·47	1·03	,,
44·4	0·426	3·0	0·480	3·48	0·52	0·48	,,
47·5	0·444	3·28	0·333	3·52	0·48	0·24	Opaque
50·0	0·481	3·5	0·107	3·55	0·45	0·05	Coagulated
52·7	0·571	3·75	0·006	3·75	0·25	0·00	,,

It will be seen that the maximum hydrolysis occurred when just over two atoms of chloride of the zirconium chloride had been reacted upon, and that the rapid increase in hydrolysis during the first portion of the titration was accompanied by a corresponding change in the composition of the basic zirconium chloride actually present in the solution (columns 5 and 6). Thereafter, the composition of the basic zirconium chloride remained nearly constant and corresponded roughly with the formula $Zr(OH)_{3·5} Cl_{0·5}$ until after coagulation ensued, when it was partially decomposed by the alkali. The first half of the titration, besides yielding a rapidly increasing basic chloride, was accompanied by a gradual decrease in the amount of free acid, which tended to render the basic zirconium chloride more and more insoluble and thus produced a gradual growth in the size of the basic chloride particles. At the beginning of the titration the particles probably approximated to molecular dimensions, but as the chloride became more and more basic these exceedingly small particles coalesced to form larger and larger aggregates until they became sufficiently big to render the solution opalescent, and this process still continued through the period when the solution had become visibly and increasingly colloidal right up to the point when coagulation occurred. The table shows that the free acid had some inhibiting effect on this growth in the size of the particles, for it was only after an ap-

preciable proportion of the acid had been neutralised that the
solution became opalescent, and, after the basic chloride particles
had become uniform in composition, it was only after the amount
of free acid had been almost removed that the colloidal solution
coagulated.

Colloidality of Zirconium Chloride Solutions.

These observations seem to suggest that the nature of basic
zirconium salt solutions is essentially colloidal in spite of the fact
that many of the solutions are perfectly clear.   Müller (Z. anorg.
Chem., 1907, 52, 316) arrived at the same conclusion from a study
of the reactions of zirconium salt solutions.   The observations,
moreover, furnish an excellent example to show that the process
of precipitation is one which involves the formation of a colloidal
solution which subsequently coagulates.   In the majority of
precipitations the colloidal solution stage is so rapidly passed that
it is not observed.

Adolf and Pauli (Kolloid Z., 1921, 29, 173) found that the
hydrolysis of solutions of zirconium oxychloride, $ZrOCl_2$, of con-
centrations ranging from 0·0022 to 0·125 M., after 10 days' standing,
varied irregularly between 35 and 50 per cent.   As mentioned
above, a freshly prepared solution of zirconium chloride containing
1Zr : 1·737Cl was hydrolysed to the extent of 54 per cent., whereas
in the solution containing the basic chloride having the same
composition in the titration the hydrolysis was considerably greater,
viz., 83·1 per cent.   In the latter case, the solution was opalescent
and therefore contained larger particles than the corresponding
clear solution.   Thus the degree of hydrolysis appears to be a
function of the size of particle, and consequently the smaller
amount of hydrolysis in the clear solutions of Adolf and Pauli
must have been due to the presence of particles which had been
rendered small by the solvent-effect of the free acid.   They
prepared zirconium oxide hydrosols by dialysis, which contained
appreciable amounts of chloride ;   one contained 0·33 atom of
chlorine and the other 0·26 atom to each atom of zirconium.   Both
sols were hydrolysed to small extents, viz., 0·9 and 0·6 per cent.
It is important to note that, although the concentration of free
acid was small, there was a relatively large concentration of
chloride ions, 41 and 37 per cent. respectively of the total chlorine
content.   The ratio of Zr : Cl in these hydrosols corresponds
to points on the titration curve lying between those representing
3·5 and 3·75 equivalents of sodium hydroxide, i.e., just after
coagulation had taken place.   The amount of free acid was of

the same order in both the colloidal solutions and the mother-liquor in which the basic zirconium precipitate was suspended. The large concentration of chloride ions in the colloidal solutions shows that the basic chloride particles do dissociate in some way.

Anomalous Behaviour of Zirconium Sulphate Solutions.

Solutions of zirconium sulphate behave towards some reagents in a manner quite different from that of solutions of either the chloride or the nitrate, so much so that Ruer (*Z. anorg. Chem.*, 1904, **42,** 85) and others have postulated that the sulphate must exist in solution as a complex sulphuric acid in which the zir-conium is present in a complex anion and thereby escapes precipi-tation. Thus oxalic acid and alkali metal oxalates fail to precipi-tate it, and sulphites only precipitate it slowly and incompletely. If potassium chloride be added to a zirconium sulphate solution, either before or after the addition of sodium oxalate, the solution becomes readily precipitable. Another point of difference is the behaviour towards sodium tartrate. Zirconium chloride yields a precipitate with sodium tartrate, readily soluble in excess, as compared with the precipitate which is obtained from zirconium sulphate solution, which dissolves only on boiling or on prolonged standing. The precipitate in the latter case is mainly basic zir-conium sulphate. Chauvenet (*Ann. Chim. Phys.*, 1920, **13,** 82) titrated several zirconium salt solutions conductometrically, and found that the titration curves, instead of being straight lines as in acid-alkali neutralisations, were slightly curved, such that the tangents drawn to the curves at each end intersected at points corresponding to approximately two equivalents of alkali. This he claimed to be evidence for the existence of the " zirconyl," $ZrO\cdot\cdot$, radical. The data given in the previous table show that during the addition of the first two equivalents of alkali the basic chloride undergoes hydrolysis and the remaining two equivalents cause little variation in its composition, $Zr(OH)_{3\cdot5}Cl_{0\cdot5}$, except at the end. These two processes, which took place in the precipi-tation from zirconium chloride solution, undoubtedly account for the change in the slope of Chauvenet's curve, which had there-fore nothing to do with an alleged zirconyl radical. Chauvenet also titrated a solution of zirconium sulphate by the conductivity method and obtained the point of minimum conductivity when 3 equivalents of alkali had been added ; this he claimed to be due to the separation of a definite basic sulphate, $ZrOSO_4,ZrO_2$. He also claimed that an inflexion was produced when two equivalents of alkali had been added, which pointed to another definite basic

salt, zirconyl sulphate, $ZrOSO_4$.   In view of the peculiar properties shown by zirconium sulphate and of the contentions of Chauvenet, it was decided to subject the sulphate to titration with the hydrogen electrode.

The zirconium sulphate had the composition

$$ZrO_2,2\cdot10SO_3,2\cdot29H_2O,$$

from which a $0\cdot01301$ M.-$Zr(SO_4)_2$ solution was prepared at room temperature ; therefore 100 c.c. of the solution contained uncombined sulphuric acid equivalent to $2\cdot56$ c.c. of N/10-alkali.   The curve showing the titration with N/10-sodium hydroxide of 100 c.c. of this solution at 18° is given in Fig. 65.   The first inflexion occurred when the added alkali was equivalent to 3 mols. to 1 mol. of zirconium sulphate.   At this point precipitation was complete and the solid had the composition $ZrO_2,\frac{1}{2}SO_3$.   The further addition of alkali (up to $50\cdot4$ c.c.) caused its partial decomposition and the mother-liquor became alkaline.   The composition of the precipitate must then have been $ZrO_2,0\cdot16SO_3$, but the slope of the curve during the addition of the next few c.c. of alkali shows that some alkali was still being withdrawn from the solution and utilised in decomposing the precipitate still more.   The sulphate solution, unlike that of the chloride, began to yield a precipitate immediately the alkali was added.   It is curious that by warming zirconium sulphate solution it may be made strongly basic by means of alkali without the separation of a precipitate, the solution remaining quite clear.   The dotted curve given in Fig. 65 is the titration curve of 100 c.c. of sulphuric acid containing $41\cdot6$ c.c. of N/10-sulphuric acid, equivalent in concentration to three-quarters of the combined acid in the zirconium sulphate solution together with the small amount of free sulphuric acid. The two curves are nearly coincident over the first half of the zirconium sulphate curve, but vary a little during the addition of the third equivalent.   The curves show therefore that the zirconium sulphate solution contained a basic sulphate and free sulphuric acid in approximately the proportions 1 mol. of ZrO_2, $\frac{1}{2}SO_3$ to $1\frac{1}{2}$ mols. of H_2SO_4.   The addition of alkali had the main effect of neutralising the free sulphuric acid, with the consequence that the basic sulphate with which it had existed in some kind of equilibrium was precipitated.   The curves give no evidence of Chauvenet's so-called zirconyl sulphate, but do confirm his observation of the precipitation of a basic sulphate of approximately the composition $ZrO_2, \frac{1}{2}SO_3$.   Further work, however, is necessary on the lines of the phase rule before its individuality can be established.
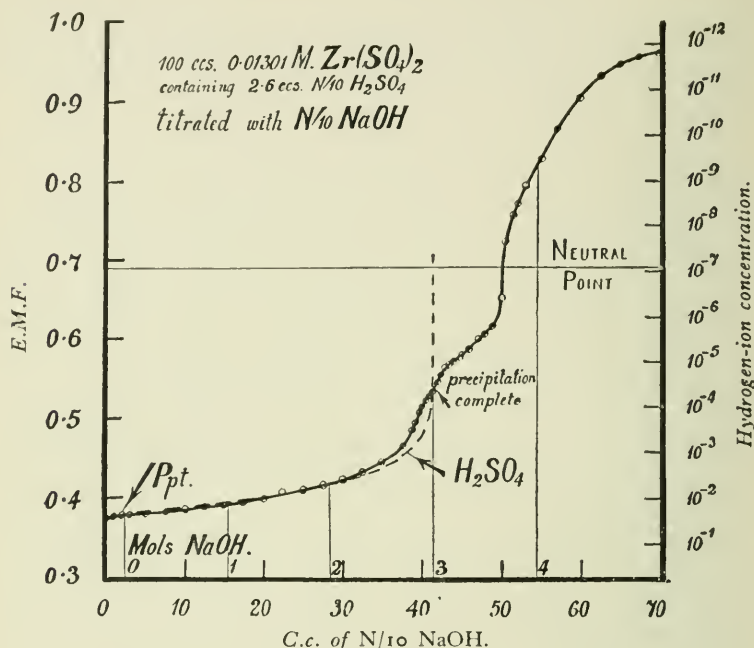
FIG. 65.—Precipitation of Basic Zirconium Sulphate.

TABLE 78.

RARE-EARTH SOLUTIONS TITRATED AT 18° C.

Titration and Curve No.	Solution Titrated (100 c.c.).	Normality of NaOH.	Precipitation.		
			Began.		Ended.
			pH.	C.c. of NaOH.	Equivs. NaOH.
1	0·0133 M.-La(NO$_3$)$_3$	0·090	8·35	1·0	2·60
2	0·0133 M.-CeCl$_3$	0·1018	7·41	1·8	2·61
3	(1) 0·0163 N-HCl	0·1018	—	—	—
	(2) 0·0114 M.-PrCl$_3$	—	7·05	18·2	2·45
4a	0·0133 M.-Nd(NO$_3$)$_3$	0·1018	7·00	0·8	2·38
4b	(1) 0·0154 N-HCl	0·1018	—	—	—
	(2) 0·0114 M.-NdCl$_3$	—	7·02	18·0	2·53
5	0·0133 M.-YCl$_3$	0·090	6·78	1·0	2·36
6	(1) 0·0140 N-HCl	0·1018	—	—	—
	(2) 0·0121 M.-SaCl$_3$	—	6·83	16·1	2·48

The view that these somewhat inert basic zirconium sulphate particles exist in solution in equilibrium with hydrolysed sulphuric acid gives an explanation of the abnormal behaviour of reagents towards zirconium sulphate solutions, especially that of sodium tartrate in precipitating the basic sulphate in such a state that it is not readily soluble in excess of the reagent.

The Cerite Group of Rare Earths and Yttrium.

A series of hydrogen electrode titration curves were obtained (Britton, *J. Chem. Soc.*, 1925, **127**, 2142) showing the changes in
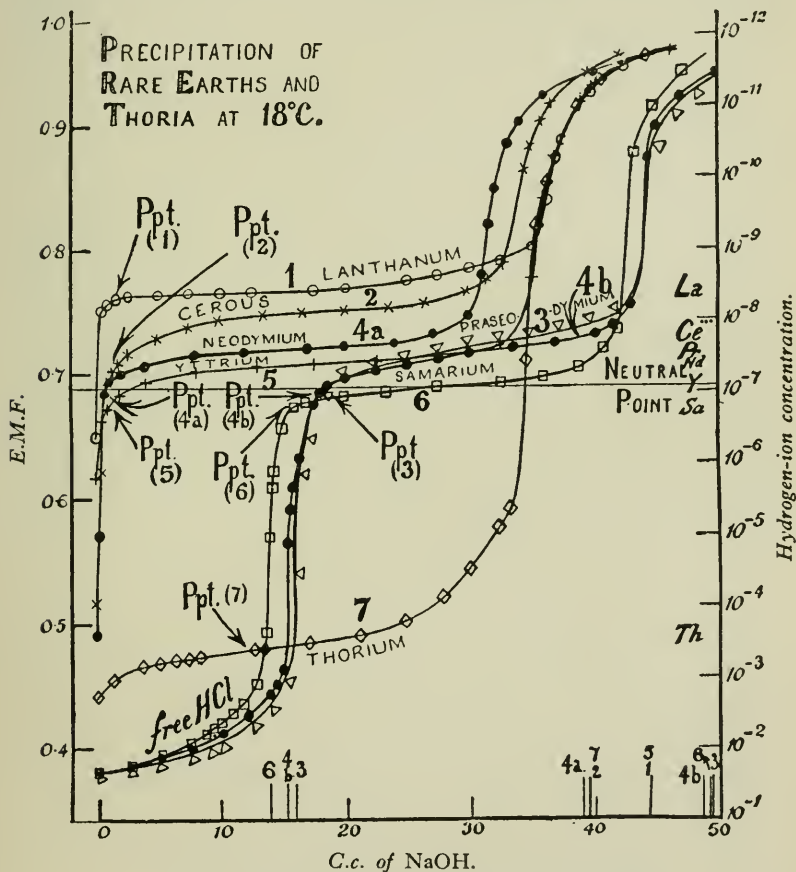
FIG. 66.—Precipitation of Thoria and Rare Earths.

hydrogen-ion concentration undergone during the precipitation of certain rare earths. Particulars of the solutions are given in Table 78, and the curves in Fig. 66.

As thoria occurs with the rare earths in monazite sand, the titration curve (No. 7), of 100 c.c. of 0·01 M.-thorium chloride solution with 0·1016 N-sodium hydroxide has been included in order that the precipitation pH of thoria might be compared with those of the rare earths. The great difference in the hydrogen-ion concentrations accounts for the ease with which thoria can be separated from the rare earths of the " cerite " group by those methods which depend on the change in pH. Knowing the respective hydrion concentrations it is possible to effect the separation of thorium hydroxide from the rare earths by carefully varying the pH of the solution by means of alkalis and suitable indicators. The hydrogen-ion concentrations may be varied : (a) by using reagents which impart hydrion concentrations to the solutions greater than those to be attained for the precipitation of the rare earths but less than that for thorium hydroxide, and (b) by fractional precipitation with bases which produce pH's which are greater than those produced by the bases to be separated. Methods employing the former device need no control, but those based on the latter principle must be controlled, either as regards the hydrion concentrations by means of indicators or electrometric measurements, or as regards the fractions themselves by determining their chemical equivalents ; which is the method usually adopted.

The hydrogen-ion concentrations which were necessary for the precipitation of lanthanum and cerous hydroxides (curves 1 and 2) were appreciably less than those required for the other four earths. The differences in pH at which the earths praseodymia, neodymia, yttria, and samaria were precipitated, although very small in the case of the first three, were sufficient to indicate that these are precipitated in the order given, which happens to the order usually claimed. The closeness of the hydrion concentrations prevailing throughout the precipitations of the hydroxides of praseodymium, neodymium, and yttrium shows that a separation of these three earths by a hydrogen-ion concentration method is impracticable. The strongest base of the yttrium group is generally stated to be yttria, and according to these measurements, it appears to have a strength of the order of that of " didymia." Curves 4a and 4b, illustrating the respective titrations of the nitrate and chloride of neodymium, show, contrary to the observations of Hildebrand (J. Amer. Chem. Soc., 1913, **35**, 847), that the hydrogen-ion concentration required for the precipitation of neodymium hydroxide is quite independent of the nature of the anion.

The lower value obtained for the nitrate solution must have been due to the use of an electrode whose hydrogen was catalytically reducing the nitrate.

The hydrogen-ion concentrations at which lanthanum and cerous hydroxides are precipitated are a little greater than that necessary for manganous hydroxide. It was therefore thought that the presence of ammonium chloride in sufficient quantity might prevent their precipitation with ammonium hydroxide (see p. 257). Calculation shows that, for each molecule of ammonia, 14 and 32 molecules, respectively, of ammonium chloride should be sufficient to prevent the precipitation of lanthanum hydroxide and cerous hydroxide. Actually, ammonium chloride has some inhibiting effect on the precipitation of the two hydroxides, and when the proportion of ammonium chloride to ammonium hydroxide is large, as indicated by the calculations, the precipitation can be entirely prevented.

Precipitation of Mercuric, Cadmium, Lead, Silver, Cupric, Uranic, and Ferric Hydroxides, investigated with the Oxygen Electrode.

On account of the inapplicability of the hydrogen electrode in solutions of salts of the above bases, resort was made to the oxygen electrode (*J. Chem. Soc.*, 1925, **127**, 2148), and in order to get an approximate idea of the variations which occurred in the concentrations of hydrogen-ions, the salt solutions were acidified to known concentrations whose pH values could be calculated. They were titrated with alkali, and from the excesses added the final pH values could also be found. The voltages of the oxygen electrode-normal calomel electrode combination found for each titration could then be resolved into pH values merely by simple proportion (*cf.* p. 76). With the exception of the silver nitrate

TABLE 79.

Titra-tion and Curve No.	100 c.c. of Solution contained :		NaOH Normality.	Precipita-tion pH (approx.).	Equivs. NaOH for Complete Precipitation.
	Free Acid.	Salt.			
1	0·0212 N-HCl	0·02 M.-HgCl$_2$	0·1018	7·4	1·5
2	0·0199 N-H$_2$SO$_4$	0·02 M.-CdSO$_4$	0·1018	6·7	1·5
3	0·0202 N-HNO$_3$	0·02 M.-Pb(NO$_3$)$_2$	0·1005	6·0	1·5
4	0·0202 N-HNO$_3$	0·02 M.-AgNO$_3$	0·1018	—	2·0
5	0·0199 N-H$_2$SO$_4$	0·02 M.-CuSO$_4$	0·1018	5·4	1·47
6	0·0149 N-HNO$_3$	0·00833 M.-U(NO$_3$)$_6$	0·1005	4·2	5·93
7	0·0202 N-HCl	0·0133 M.-FeCl$_3$	0·1005	opalesc. 2·3 coag. 6·6	2·35 2·85

titration, for which a saturated potassium nitrate solution had to be used as the junction liquid for obvious reasons, these proportional pH scales might be considered as indicating values with an accuracy of about a 0·5 pH unit.

It will be seen from Table 79 that under the conditions of gradual precipitation the hydroxides are, in general, not obtained, but precipitates containing basic salts. Thus, copper sulphate solutions when subjected to careful treatment with alkalis, in quantities less than three-quarters of the amounts requisite for the complete decomposition of the salt, yield precipitates of $4CuO$, $SO_3,4H_2O$, which has been proved by phase rule methods to be a definite basic salt (Britton, *J. Chem. Soc.*, 1926). It may be that the precipitates obtained in titrations 1, 2, and 3 were basic salts of similar composition, *viz.*,

$$3HgO,HgCl_2,xH_2O$$
$$3Cd(OH)_2,CdSO_4,xH_2O$$
$$\text{and } 3Pb(OH)_2,Pb(NO_3)_2,xH_2O.$$
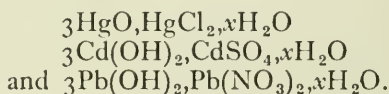
A basic precipitate was not obtained from a silver nitrate solution, and the uranic and ferric hydroxide precipitates contained only relatively small amounts of undecomposed salt. Fig. 67 shows in titration No. 6 precipitation was complete when 64 c.c. of alkali had been added as compared with the 64·7 c.c. which were required for the complete formation of uranic hydroxide. Hence the precipitate was uranic hydroxide containing a very small quantity of undecomposed nitrate. Text-books state that alkalis precipitate " diuranates " and not uranium hydroxide ; *e.g.*, with sodium hydroxide, the precipitate is stated to be $Na_2U_2O_7$ (compare Roscoe and Schorlemmer's *Treatise*, Vol. II., p. 1154, revised 1923). Jollibois and Bosnet (*Compt. rend.*, 1922, **174,** 1625) found that the precipitates produced by the action of sodium hydroxide on uranyl nitrate solutions contained no nitrate ; the small quantities of sodium hydroxide present, varying from 1·2 to 8 per cent., they considered to be adsorbed.

The approximate pH values at which the various precipitates began to form from the dilute solutions used are given in Table 80. Although the oxygen electrode is of considerable service in electrometric titrations, the pH values, which its potentials may be considered to show, are far from satisfactory. It is desirable that the correct pH ranges of precipitation of these bases should be measured by more accurate methods, *e.g.*, with the glass electrode, or when applicable, with the quinhydrone electrode.
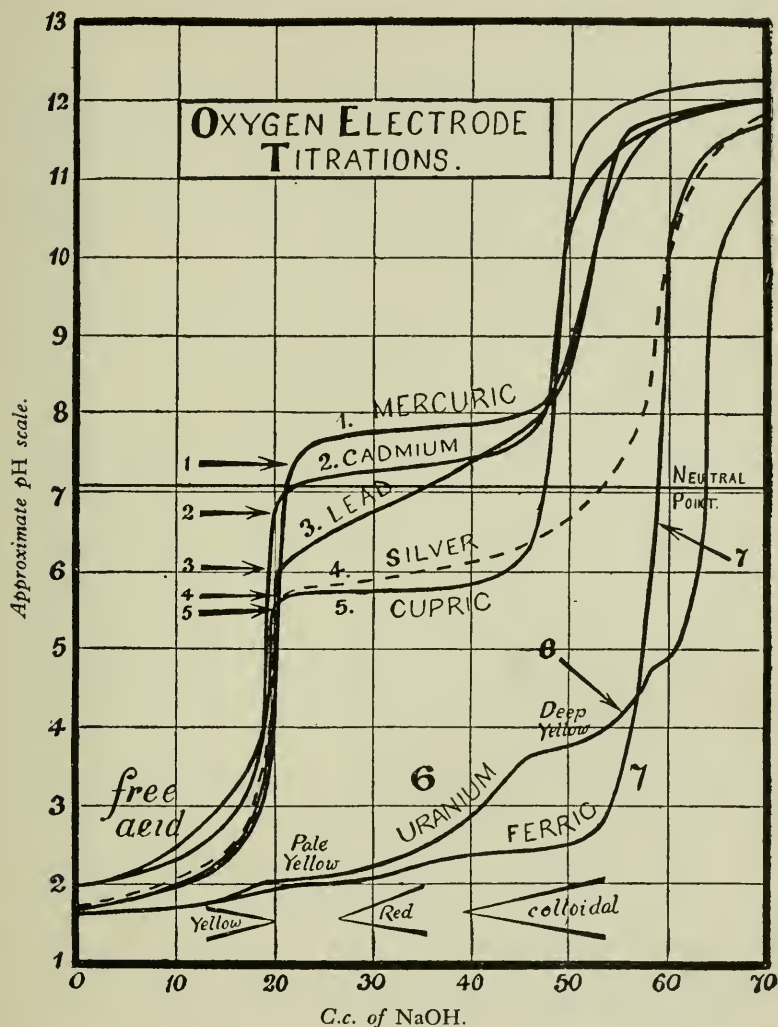
FIG. 67.—Oxygen Electrode Titrations involving Precipitations.

Arrangement of Metals in the Order of the Hydrogen-Ion Concentrations required for the Precipitation of their Hydroxides.

It was stated on page 248 that no principle has yet been found which leads to a satisfactory arrangement of the metals such that the order is that of the basic strengths of their hydroxides.   The

titrations described in the foregoing pages show that for each hydroxide there is a narrow range of hydrogen-ion concentration within which its precipitation normally takes place from dilute solutions. It is true that the majority of the hydroxides are thrown out of solution as basic precipitates, but the hydrogen-ion concentrations at which these are precipitated probably do not differ greatly from those of the particular hydroxides. Table 80 gives the metals

Table 80.

Hydroxide Precipitation pH's from Dilute Solutions.

Hydroxide.

Magnesium	.	.	10·5	Lead	.	.	6·0
Silver	.	.	9 (?)	Beryllium	.	.	5·7
Manganous	.	.	8·5–8·8	Ferrous	.	.	5·5
Lanthanum	.	.	8·4	Cupric	.	.	5·3
Cerous	.	.	7·4	Chromium	.	.	5·3
Mercuric	.	.	7·3	Zinc	.	.	5·2
Praseodymium		.	7·1	Uranic	.	.	4·2
Neodymium	.	.	7·0	Aluminium	.	.	4·1
Samarium	.	.	6·8	Thorium	.	.	3·5
Cobalt	.	.	6·8	Stannous	.	.	2 (?)
Yttrium	.	.	6·8	Zirconium	.	.	2 (?)
Cadmium	.	.	6·7	Ferric	.	.	2 (?)
Nickel	.	.	6·7				

in the order of the hydrogen-ion concentrations at which their respective hydroxides are precipitated from dilute solutions. Although it is not certain that this order is that of the actual basic strengths of the hydroxides, it can be stated, as will be shown later, that it is these hydrogen-ion concentration relationships which underlie many of the reactions of the various metallic salt solutions.

It was pointed out on page 249 that in the case of sparingly soluble bases an arrangement in the order of their affinity constants was not possible, owing to the fact that, although their solubility products could sometimes be determined, it was not usually possible to calculate the concentrations of the undissociated bases in such extremely dilute solutions.

If the order of the precipitation of the hydroxides is actually that of their basic strengths, the basic strengths of the rare earths lie between those of zinc and manganous hydroxides, and below that of magnesium hydroxide. Lanthanum hydroxide is always stated to be the strongest base of the rare earths, and the " cerite " group of hydroxides, excepting ceric hydroxide, to be the group of the strongest bases. Apart from lanthanum hydroxide and perhaps cerous hydroxide, the other earths appear to be quite moderate in strength and are comparable with cobalt and nickel

hydroxides. This is contrary to the view generally held. Little in Friend's *Text-Book of Inorganic Chemistry*, 1917, Vol. IV., p. 257, states that " from general chemical and thermochemical considerations it may be concluded that they [the rare earths] are stronger than magnesia, but weaker than the alkaline earths." The chemical considerations are epitomised thus : " The strongly ignited oxides are readily soluble in mineral acids, several of them combine directly with water and absorb carbon dioxide from the air, and all of them liberate ammonia from cold solutions of ammonium salts. Normal salts of numerous weak acids, *e.g.*, chromic, carbonic, are readily prepared." If the hydrogen-ion concentration relationships do give the true order of basic strengths, then zinc hydroxide is a weaker base than either of the tribasic hydroxides of the " cerite " elements ; yet its oxide after ignition is readily soluble in mineral acids. The behaviour of the rare earths towards cold ammonium salt solutions is misleading. The fact that a base forms well-defined salts with weak acids probably offers no clue to its strength, if those salts happen to be almost insoluble. This is the case with the carbonates and chromates of the rare earths (*vide* Britton, *J. Chem. Soc.*, 1924, **125,** 1875). Thus thorium hydroxide is an exceedingly weak base, but under certain conditions it forms an extremely well-defined chromate ; under other conditions it behaves like other weak bases and gives precipitates which are indefinite and basic (*vide* Britton, *ibid.*, 1923, **123,** 1429). The power to form well-defined salts with weak acids seems to be a property inherent in an element in conferring a small solubility on a salt and probably has nothing whatsoever to do with its power to form a strong base. There is no marked difference between the stability of acetates and of the metals whose hydroxides are precipitated at comparable hydrogen-ion concentrations, *e.g.*, zinc, cobalt, nickel and cadmium.

Vesterberg found (*Svensk. Kemi Tidskrift*, 1917, **29,** 101 ; *Z. anorg. Chem.*, 1917, **99,** 11, 22) that equally concentrated solutions of lanthanum acetate and ammonium acetate were equally hydrolysed. This led him to conclude that the strengths of lanthanum hydroxide and ammonium hydroxide are nearly the same. Fig. 66 shows that lanthana was precipitated from an alkaline solution the hydrogen-ion concentration of which varied from $10^{-8.35}$ to 10^{-9}. The very small concentration of lanthanum hydroxide therefore imparts to the solution a hydroxyl-ion concentration of the order of 10^{-5}, a concentration which is restricted by the small solubility of the lanthana. The actual amount of dissolved lanthanum hydroxide is too small for accurate estimation, and consequently it is not possible to calculate its degree of

dissociation and its basicity constant, nor to compare the hydroxyl-ion concentrations given by equal concentrations of ammonia and lanthana. Theoretically, it is possible to compare them from a knowledge of the degrees of hydrolysis of solutions of their respective salts under absolutely identical conditions. It is extremely doubtful whether this is accomplished by Vesterberg's method on account of the different nature of the two bases, for on extracting the hydrolysed acid from a lanthanum acetate solution with ether the equilibrium is disturbed in some unknown manner. The lanthanum hydroxide, unlike the ammonium hydroxide in the case of the ammonium acetate solution, will tend to become precipitated or to pass into a colloidal solution, and thereby give rise to increased hydrolysis.

An arrangement now widely adopted is that based by Abegg and Bodländer (*Z. anorg. Chem.*, 1899, **20,** 453) on their theory of electroaffinity, which states that the electrolytic potential constitutes an approximate measure of the basic strength of the metal. Comparison with the present arrangement brings out the following important differences. According to the position of aluminium in the table, aluminium hydroxide is an extremely weak base, weaker than chromium hydroxide, yet aluminium occurs higher than chromium in the Electropotential Series. There is no doubt that both aluminium and chromium hydroxides are much weaker bases than manganous hydroxide, and this is also indicated by the present scheme, but according to the electropotential series they both are placed above manganese. Heyrovský (*Proc. Roy. Soc.*, 1923, *A*, **102,** 628) has pointed out that the thallous potential is small, which necessitates placing thallium relatively close to hydrogen in the electropotential series, in spite of the fact that thallous hydroxide is a strong base and is not precipitated by alkalis. If it be assumed that the electrolytic potentials of metals under identical conditions are a measure of their electroaffinities, *i.e.*, the free energies by which the elements take up electric charges, it cannot be concluded, as was admitted by Abegg and Bodländer, that the potentials as determined are in any way parallel to the electroaffinities, for nothing is known of the relative atomic solubilities of the various metals in water. Unless it is known that the number of atoms of the different metals which pass into solution is the same, no guarantee can be obtained that an arrangement accruing therefrom is in any way true. Heyrovský attempted to amend the above method by introducing such factors as the mass of the cation, and obtained an order which he considered to be satisfactory. Heyrovský's system indicates that lead hydroxide is a stronger base than magnesium hydroxide, and that mercuric

oxide is a very weak base, weaker than zinc hydroxide. Table 80 suggests the contrary in both cases. It is well known that water becomes alkaline (to litmus) when shaken with mercuric oxide, but remains neutral when shaken with zinc oxide. It is probable that the pH series of metallic hydroxides is the most satisfactory arrangement which has yet been advanced, and from the hydroxide precipitation pH, it is an easy matter to state whether or no a precipitate will be produced when solutions of their respective salts are reacted upon by certain reagents. The salt solutions of the bases are found to be hydrolysed to a greater extent, as the hydroxide pH becomes lower and lower, so much so, that those of the bases at the bottom of the pH series are very considerably hydrolysed. It is with solutions of such salts that colloidal effects become apparent, and delay the appearance of a precipitate until a proportionately large amount of precipitant has been added. For such bases, it is not easy to assign with any certainty the pH at which precipitation actually does take place.

It will be shown in the next chapter that in the precipitation of basic carbonates, chromates, borates and silicates, the main factor which brings about precipitation is the attainment of the hydroxide pH, except in the case of those silicates which were precipitated from alkaline solutions.

It is interesting to note that, in general, when reagents, which were incapable of setting up pH's high enough for the precipitation of the hydroxides, were added to solutions, no precipitates were formed. Thus, neither potassium chromate, nor borax, when added to dilute magnesium salt solutions imparted to them a pH as high as 10·5, and therefore could not cause precipitation.

Controlled Separations.

These hydroxide precipitation pH's may be used to facilitate many separation processes, and, indeed, the separations may even be controlled by using a suitable indicator of the hydrogen-ion concentration, either colorimetric or electrometric. Thus Ralston (*Trans. Amer. Electrochem. Soc.*, 1923, **43**, 87) found the oxygen electrode to be of considerable use for this purpose in the hydrolytic purification of electrolytes, such as the freeing of copper sulphate from traces of ferric hydroxide. Many analytical separations have been so worked out that the procedures themselves control automatically the hydrogen-ion concentration that the pH for one hydroxide is exceeded, whereas that of another is not. This is especially the case in the use of ammonium chloride, for, as shown on page 257, the buffering effect produced by 0·08 molecule to 1 of

ammonium hydroxide is all that is necessary to prevent the attainment of the magnesium hydroxide pH, and 4·5 molecules to prevent the precipitation of manganous hydroxide. Again, in either the basic acetate or basic succinate methods of separating iron from manganese, the buffering action of the partly-neutralised acid, maintains a hydrogen-ion concentration of about pH 5, which compels the ferric hydroxide to be precipitated, pH 2, but is sufficient to retain the manganous hydroxide in solution, as it is not precipitated until nearly pH 9 is reached. Lundell and Knowles (*J. Amer. Chem. Soc.*, 1923, **45**, 676) have shown that the separation may equally well be performed by fractional precipitation with ammonia in the presence of ammonium chloride, the precipitation of the ferric hydroxide being ensured by rendering the solution just alkaline to methyl red, *i.e.*, about pH 6·3. Darbishire (*Industrial Chemist*, 1927, 172) has pointed out that the standard method of separating manganese from both iron and aluminium in, for example, the analysis of manganiferous silicates by precipitating the latter two as basic acetates from very dilute neutral solutions by boiling with sodium acetate involves a difficult precipitation, a reprecipitation, tedious filtrations, and is such as can scarcely be regarded as accurate except when carried out with considerable care and skill. When the estimations are to be carried out volumetrically, he advocates the use of finely powdered zinc oxide as separating agent, which precipitates the aluminium and ferric hydroxides and leaves the manganese in solution. The principle underlying this procedure is apparent from Table 80. Zinc hydroxide sets up a pH of 5·2, and thus falls between that of manganous hydroxide, pH 8·8, and aluminium hydroxide, pH 4·14, and ferric hydroxide, pH 2. It is essential that all iron in the solution shall be in the oxidised condition, for ferrous hydroxide is precipitated at pH 5·5. Lassieur (*Ann. chim. annal.*, 1926 [ii], **8**, 97 ; *Compt. rend.*, 1926, **182**, 384) has recently shown that magnesia can be separated from alumina by means of ammonia if only sufficient be employed to raise the pH to 7, as may be indicated by the appearance of the blue tint of bromothymol-blue ; beyond pH 7 some magnesium hydroxide was carried down. The table also explains why mercuric oxide can be used as a separating agent for various bases. Thus E. F. Smith and Heyl (*Z. anorg. Chem.*, 1894, **7**, 87) showed that mercuric oxide caused the complete precipitation in the cold of ferric, aluminium, and chromium hydroxides, the partial precipitation of zinc, cobalt, nickel, uranium, beryllium, cerous, and lanthanum hydroxides, and failed to precipitate manganous hydroxide. The table shows that the hydrogen-ion concentration peculiar to mercuric oxide is greater

than that required to precipitate manganous hydroxide, is approximately equal to that required for lanthana, is somewhat less than that required by those hydroxides which were partly precipitated, and is considerably less than that of the three bases which were completely precipitated.

Fig. 68 gives the types of curves which are obtained when the changes in hydrogen-ion undergone during separations are followed electrometrically. Thus the curve A corresponds to the pH
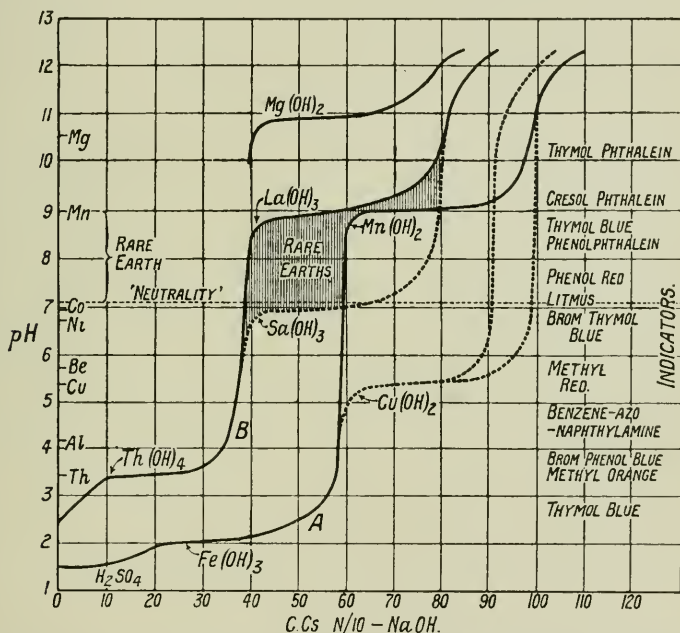
Fig. 68.—Curves showing how Hydroxides may be separated by taking advantage of variations in hydrogen-ion concentrations on addition of alkali.

changes when N/10—NaOH is added to a solution, about 100 c.c. in volume, and containing sulphuric acid equivalent to 20 c.c. of alkali, ferric sulphate to 40 c.c., and manganous sulphate to 40 c.c., or in case of dotted curve copper sulphate equivalent to 40 c.c. in place of the manganous salt. These curves are diagrammatic only for the hydrogen electrode will not function in presence of either ferric or copper salts. The oxygen electrode, however, may be used to follow the two separations, and though the pH's may not be calculated from the voltages with any degree

of accuracy, the sudden variations produced in hydrion concentration when one hydroxide has been completely thrown down will be indicated by a steep inflexion, and thus will indicate when one precipitate may be filtered off. It should be mentioned that when the weaker bases, such as ferric hydroxide, stannous hydroxide and zirconia, are dissolved in hydrochloric acid there is a pronounced tendency for the precipitate to remain in colloidal solution, which does not coagulate until somewhere in the region of pH 7 has been attained, but this does not obtain with sulphuric acid solutions. It will be seen from the diagram that the colour-change of methyl red corresponds with that pH when all the iron has been precipitated. The iron-copper separation, however, involves pH's which are probably too close together to be regulated by any other method than the electrometric method, with the oxygen electrode as used by Ralston. Curve B corresponds to mixtures of thorium salt, equivalent to 40 c.c. of alkali, and a rare earth salt, say, lanthanum sulphate or samarium sulphate, equivalent to 40 c.c. The precipitation pH's of other rare earths which have been investigated fall within the shaded area lying between the lanthanum and samarium curves. Hence the thoria may be separated by neutralising the solution to methyl red. Reagents which have been used to effect this separation and which automatically control the pH in order that it may fall between the precipitation pH's are zinc oxide, pH 5·2 ; copper oxide, pH 5·4 ; certain very weak organic bases, *e.g.*, quinoline, *p*-toluidine (Jefferson, *J. Amer. Chem. Soc.*, 1902, **24**, 540 ; Allen, *ibid.*, 1903, **25**, 421 ; Hartwell, *ibid.*, p. 1128) ; sodium thiosulphate, and buffered solutions of hydrazoic acid (*i.e.*, acidified sodium azide). The precipitation pH's of praseodymia, 7·05, and neodymia, 7·00, are nearly identical, and therefore explain why these earths could not be fractionally precipitated with ammonia. The difference between the pH for lanthana and that for cerous cerium is too small to permit of a separation based on this principle, but when cerium is oxidised to the ceric state, the pH of precipitation as ceric hydroxide then becomes about 3, and enables separation to be effectively carried out, and which could be facilitated considerably by the use of indicators or the oxygen electrode, the hydrogen electrode being useless in presence of ceric salts. Another separation which has been the subject of much work is that of aluminium from beryllium, these two metals occurring together in beryl, the chief source of the exceptional metal beryllium (*vide* Britton, *Analyst*, 1921, **46**, 359, 437 ; 1922, **47**, 50). Table 80 shows that the precipitation pH of aluminium hydroxide is 4·14, and of beryllium hydroxide 5·69, and the prox-

imity therefore accounts for the great difficulty in separating the two metals by a method based on this principle.

The methods recently devised by Moser, Niessner and Singer (*Monatsh. für Chem.*, 1927, **48,** 113, 673) for the analytical separation of beryllia from bases which have lower precipitation pH values than that of beryllium hydroxide are of interest. They are precipitated as tannin adsorption complexes from very dilute solutions whose hydrogen-ion concentrations have been carefully buffered so as to give pH values, which fall below that at which beryllia becomes precipitable, by means of ammonium salts, particularly the acetate, and suitable quantities of acetic acid, or, in the case of tungstic oxide ammonium nitrate and sulphuric acid. The tannin assists in the precipitation of these weak bases, which in all probability takes place at the usual hydroxide precipitation pH's, as the result of the mutual coagulation of the colloidal solutions of the tannin and the base which tend to form immediately before their precipitation actually occurs. In this way the weak bases undergo complete precipitation without the necessity of unduly raising the pH and thereby involve the precipitation of some beryllia. The precipitation curves using alkali show that the pH at which precipitation becomes complete is generally much higher than that at which the precipitate first appeared. This method was found useful for aluminium, iron (ferric), chromium, titanium (see p. 379), thorium, zirconium, tungsten, and vanadium.

CHAPTER XVI.

PRECIPITATION OF BASIC CHROMATES, BORATES, CARBONATES AND SILICATES.

THE author has correlated the formation of basic precipitates with that of the hydroxides, or rather of basic precipitates precipitated by alkalis, from dilute solutions. The solutions investigated were of the same or comparable concentrations (*J. Chem. Soc.*, 1926, 125 ; 1927, 425), and the reactions were followed with the hydrogen electrode against the normal calomel half element.

I. Basic Chromates.

Table 81 gives the particulars of the solutions and the pH's at which precipitation of basic chromates began, and these are com-

TABLE 81.

PRECIPITATION OF BASIC CHROMATES.

Solution (100 c.c.).	Precipitation of Basic Chromate began :		Precipitation of Hydroxide began :		Proportion.
	E.M.F.	pH.	E.M.F.	pH.	
o·o1 M.-ThCl$_4$	0·482	3·45	0·484	3·51	Complete
o·00667 M.-Al$_2$(SO$_4$)$_3$	0·524	4·18	0·521	4·14	,,
o·o1 M.-Cr$_2$(SO$_4$)$_3$,K$_2$SO$_4$	0·583	5·20	0·591	5·34	,,
o·o2 M.-BeSO$_4$	0·613	5·72	0·610	5·69	,,
o·025 M.-ZnSO$_4$	0·600	5·49	0·583	5·20	,,
o·0132 M.-Nd(NO$_3$)$_3$	0·657	6·48	0·686	7·00	Partial
o·0133 M.-SaCl$_3$	0·661	6·55	0·676	6·83	,,
o·0133 M.-YCl$_3$	0·672	6·74	0·674	6·78	,,
o·0247 M.-CoCl$_2$	0·688	7·01	0·676	6·81	,,
o·0200 M.-NiCl$_2$	0·674	6·78	0·666	6·66	Opalescence

pared with the respective hydroxide pH values. The titration curves are given in Fig. 69, the arrows indicating the points at which precipitates first appeared. M/10-potassium chromate was used in each titration except that of thorium chloride, in which case the concentration was M/20.

Mechanism of the Precipitation of Basic Chromates.—Table 81 shows that in the majority of the titrations a precipitate did not form until the hydrogen-ion concentration of the solution had become that at which the hydroxide separates.   In one or two cases the precipitate first formed was the hydroxide uncon-
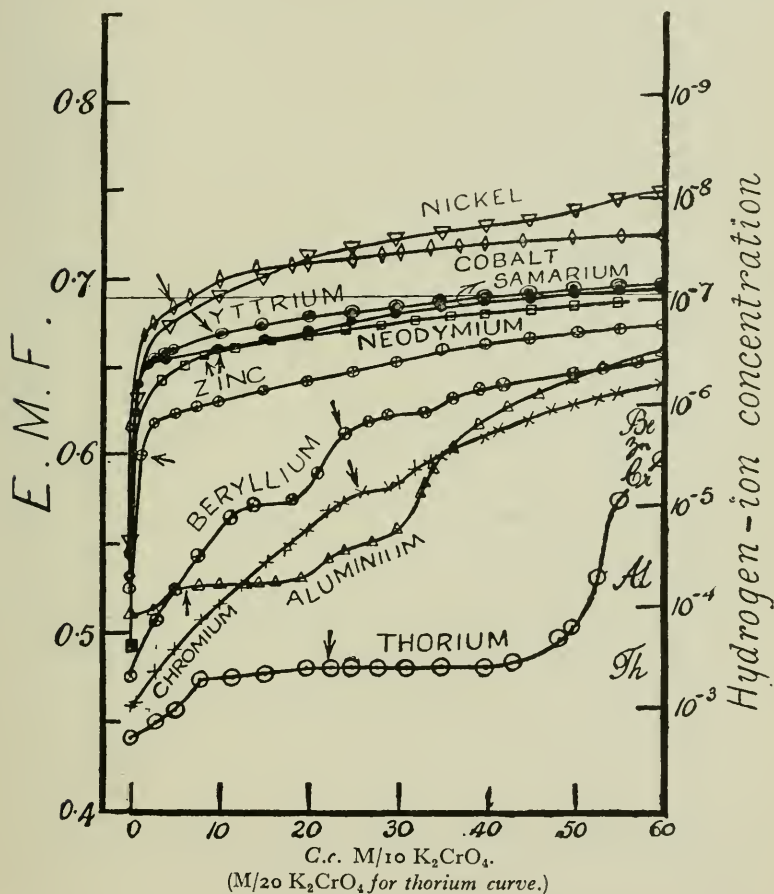
(M/20 K₂CrO₄ *for thorium curve.*)
FIG. 69.—Precipitation of Basic Chromates.

taminated with any chromate.   This was particularly the case with aluminium, the initial precipitate being aluminium hydroxide containing some unattacked sulphate.   The chief factor controlling the concentration of hydrogen-ions is the reaction whereby the acid, produced from the metallic salt by hydrolysis, and the potassium chromate generates hydrochromate-ions.   The dissocia-

of these ions is exceedingly small and is rendered still smaller by the increasing concentration of chromate-ions from the added potassium chromate. The range of hydrogen-ion concentrations which can be produced in equilibria involving chromate and hy-drochromate-ions is 10^{-5} to 10^{-8}, as may be seen from the second section of the chromic acid titration curve (p. 145). For a considerable range of equilibria the hydrogen-ion concentration remains approximately 10^{-6}. The reason why potassium chromate precipitates basic chromates from salt solutions lies in the inability of the hydrochromate-ions to react with the metallic bases and thus to maintain them in solution, except in the few instances in which insoluble normal chromates are formed. For example, consider the reactions between freshly precipitated aluminium hydroxide and the hydrochromate-ions present in potassium dichromate solutions of different concentrations. It can be shown that the pH of M/10- and M/100-$KHCrO_4$ is 3·68 and 4·18 respectively, by assuming the salts to be completely dissociated into $K^{\cdot}$ and $HCrO_4{}'$, and the latter ions to be dissociated further into an equal number of hydrogen-ions and chromate-ions. As aluminium hydroxide is precipitated at pH 4·14, it follows that at the moment of formation of the precipitate the hydroxyl-ion concentration of the solution is $K_w/10^{-4\cdot14} = 10^{-10}$. In order that the aluminium hydroxide may react with the hydrochromate-ions and consequently dissolve, the hydrochromate-ions must be capable of providing sufficient hydrogen-ions to form water with the hydroxyl-ions in the solution, $i.e.$, the product $[H^{\cdot}][OH']$ must be greater than K_w. If M/100-potassium hydrochromate solution be added to freshly precipitated aluminium hydroxide, it will set up a hydrion concentration of $10^{-4\cdot18}$, which, being less than the precipitation hydrion concentration, will be incapable of causing solution, or, in other words, $[H^{\cdot}][OH']$ will become equal to $10^{-14\cdot18}$, a value just less than K_w, $10^{-14\cdot14}$. With M/10-$KHCrO_4$, pH = 3·68, the hydrogen-ion concentration will be less than that necessary for the precipitation of aluminium hydroxide and consequently there will be a tendency for the aluminium hydroxide to dissolve, the product being $10^{-13\cdot68}$ which just exceeds the ionic product of water at 18°. If thorium hydroxide, however, be used, no reaction can take place, for its precipitation pH being 3·5, the product of the hydroxyl-ion concentration and the hydrion concentration arising from either M/10- or M/100-solution of the potassium acid chromate will be less than K_w.

The hydroxides occupying higher positions on the pH scale become increasingly reactive with the hydrochromate-ions, though very little reaction takes place with those hydroxides which are

precipitated from acid solutions. This is due to the fact that as soon as some hydrochromate-ions have been converted into chromate-ions, the hydrogen-ion concentration becomes considerably reduced and so prevents further reaction. As the hydrion concentration thereby produced is about 10^{-6}, its effect will be most marked with those hydroxides whose precipitation pH's are above 7. The reaction between those hydroxides, which are precipitated at pH 7 and above, and the hydrochromate radical becomes more pronounced and consequently potassium chromate causes either partial or no precipitation. Thus it is clear why potassium chromate fails to precipitate magnesium salt solutions. Magnesium hydroxide is precipitated at pH 10·5 and is therefore able to react with the ions produced in the second stage of the ionisation of chromic acid to an extent sufficient to prevent the attainment of the pH of precipitation. Manganous hydroxide, too, is sufficiently strong (pH 8·4) to enter appreciably into combination with the hydrochromate radical. No precipitate is formed when potassium chromate is added to a manganous salt solution, but after some time the solution deepens in colour and eventually a brownish-black precipitate appears. This, however, is due to oxidation of the relatively large amount of manganous hydroxide present in the alkaline solution by the chromate and to some extent by the air (Gröger, *Z. anorg. Chem.*, 1905, **44,** 453).

The latter precipitation reactions may also be considered from the point of view of the alkalinity of the potassium chromate solutions. By assuming complete ionisation of the various salts involved in the hydrolysis of potassium chromate solutions, it can be shown that at 18°, $[\text{H}^{\cdot}] = \sqrt{\text{K}_2\text{K}_w/\text{C}_{\text{K}_2\text{CrO}_4}}$, K_2 of chromic acid being $4\cdot4 \times 10^{-7}$. Therefore pH of M/10-potassium chromate is 9·75 and of the M/100-solution, 9·25. Hence the addition of potassium chromate solutions in either of these concentrations to magnesium salt solutions cannot cause precipitation, as the reactants are incapable of attaining an alkalinity corresponding to the pH of precipitation of magnesium hydroxide. On the other hand, it appears at first sight that if a dilute manganous salt solution contained (say) M/100-potassium chromate, the hydrogen-ion concentration, *viz.*, $10^{-9\cdot25}$, which the latter would impart, would be less than that at which manganous hydroxide is precipitated (pH 8·4). The reaction between manganous chloride (say) and potassium chromate involves a ready reaction between manganous hydroxide and the hydrions from the first stage of ionisation of chromic acid to form some $\text{Mn}(\text{HCrO}_4)_2$ and also the more difficult reaction with the hydrions from the second stage. The result

is that instead of the reaction being one of simple double decom-
position, thus $K_2CrO_4 + MnCl_2 = MnCrO_4 + 2KCl$, the forma-
tion of a precipitate depends on how far the following equilibrium
reaction is disturbed, $Mn(HCrO_4)_2 + Mn(OH)_2 \rightleftharpoons 2MnCrO_4 +$
$2H_2O$, which is governed, the oxidation effects which are peculiar
to manganous and cobaltous hydroxides being excluded, by the
two reactions (a) $HCrO_4' + OH' \rightleftharpoons CrO_4'' + H_2O$, and (b)
$Mn^{..} + 2OH' \rightleftharpoons Mn(OH)_2$. Equilibrium (a) is dependent on
K_2 and K_w, and equilibrium (b) on $[Mn^{..}][OH']^2$ or, more directly,
the pH of precipitation. Thus it follows that when M/10-potas-
sium chromate is added to a manganous salt solution of the con-
centration used in these titrations, the pH of the solution barely
attains the precipitation pH of manganous hydroxide and no
precipitate is at first produced. More concentrated solutions of
potassium chromate, however, effect partial but almost immediate
precipitation of basic manganous chromate.

The behaviour of potassium chromate towards nickel and
cobalt salt solutions is of interest. As shown in Table 80, nickel
hydroxide is precipitated at pH 6·66 and cobalt hydroxide at pH
6·81. Yet when M/10-potassium chromate is added to solutions
of cobalt and nickel salts partial precipitation occurs in the former
case and merely an opalescence is produced in the latter. The
nickel and cobalt curves show that potassium chromate produces
hydrion concentrations less than those at which the respective
hydroxides are precipitated by alkali. The partial precipitation
of cobalt is probably due to the tendency of cobalt hydroxide to
oxidise. Gentle warming of the nickel solution is sufficient to
cause precipitation.

The curves showing the course of precipitation of the basic
chromates of neodymium and samarium have been included, for
unlike the other metals, except thorium, they form well-defined,
difficultly soluble salts and thus the precipitation of one or the
other is determined by (a) the hydrogen-ion concentration, and
(b) the solubility of the normal chromate.

These hydrogen-ion relationships of the various hydroxides ex-
plain why solutions of potassium dichromate, in spite of their pH's
being greater than the precipitation pH's of certain hydroxides, fail
to cause the precipitation of basic chromates, except from zirconium
salt solutions ; and even in this case it is far from complete.
Unless concentrated solutions be used, in which case the normal
thorium chromate may be precipitated, the addition of potassium
dichromate to thorium salt solutions fails to give a precipitate,
although the pH of the dichromate solution itself is greater (3·68–
4·18 for solutions ranging from 0·1 M. to 0·01 M.) than the hydrox-

ide precipitation pH 3·5. Potassium dichromate behaves, towards a weak base like thorium hydroxide, as a salt of a strong mono-basic acid containing no reactive hydrogen atom, and on addition to a thorium salt solution merely sets up an equilibrium, $ThCl_4 + 4KHCrO_4 \rightleftharpoons Th(HCrO_4)_4 + 4KCl$, in which the thorium salt is largely hydrolysed, and thereby maintains a hydrion concentration in the solution which is much greater than that required for the precipitation of the hydroxide. An excess of potassium dichromate will have a buffering effect on the hydrolysed chromic acid, but, as the first section of the chromic acid titration curve shows, the excess would have to be considerable before the hydrogen-ion concentration could be reduced to pH 3·5.

Detailed Study of the Precipitation Reactions, Thorium.

Partial precipitation results when either M/100-thorium nitrate or chloride solutions are treated with M/20-potassium chromate in the stoichiometrical amounts, and the precipitates contained thoria and chromic anhydride in the molecular ratio of 1 : 1·38. Fig. 69 shows that 22·7 c.c. of M/20-potassium chromate caused the attainment of the hydroxide precipitation pH, at which point basic thorium chromate began to be precipitated. The next 30 c.c. caused little change in pH, but soon afterwards a rapid diminution in hydrogen-ion concentration occurred which marked the end of precipitation. On comparing the inflexion thereby produced with that in the neutralisation curve of chromic acid, it will be observed that it indicates the first stage of neutralisation of all the free chromic acid present in the solution, $KHCrO_4$ being formed. The reaction may be regarded as two simultaneous reactions : first, the gradual hydrolysis of the thorium salt thus, $ThCl_4 + 4H_2O \rightarrow Th(OH)_4 + 4HCl$, and, secondly, $4HCl + 4K_2CrO_4 \rightarrow 4KCl + 4KHCrO_4$.

As stated above, it would be expected that thorium hydroxide would show a negligible tendency to react with the small concentrations of hydrions which arise from the dissociation of hydro-chromate ions. Yet the thorium hydroxide which was precipitated contained appreciable amounts of chromic anhydride. Two reasons may be offered : (a) co-precipitation of thorium chromate, and (b) adsorption of chromic anhydride, through chemical forces at play between the weak base, thorium hydroxide, and the weak acid, $HCrO_4'$. The precipitates, apart from being yellow, resembled thorium hydroxide and appeared to contain no crystalline thorium chromate. Thorium chromate is much more soluble than the hydroxide, and seeing that the thorium- and chromate-ion

concentrations were insufficient to produce a precipitate of the normal chromate before the hydroxide precipitation pH was attained, it appears improbable that the basic chromate contained any normal chromate. The large chromic anhydride content of the basic precipitate was probably caused by a process akin to adsorption in which the chemical tendencies of the weak acid and the weak base played an important part.

An approximate estimate of the composition of the precipitate may be obtained from the titration curve. Precipitation was complete when 53 c.c. of M/20-potassium chromate had been added, *i.e.*, an amount corresponding to the mid-point of the inflexion. If thorium hydroxide alone had been precipitated, then, as shown by the previous equations, 4 mols. of potassium chromate to 1 mol. of thorium chloride would have been required, or 80 c.c. in the titration ; as compared with 2 mols., or 40 c.c. of M/20-potassium chromate, if the normal chromate had been formed. But actually 53 c.c. were required, and therefore by alligation the basic chromate precipitate must have contained $27Th(CrO_4)_2, 13Th(OH)_4$, or $ThO_2, 1 \cdot 35CrO_3$. The precipitate contained $54 \cdot 55$ per cent. of ThO_2 and $28 \cdot 47$ per cent. of CrO_3, and therefore agreed with the formula $ThO_2, 1 \cdot 38CrO_3, 4 \cdot 57H_2O$, which is similar to that suggested by the curve.

Aluminium.—Precipitation began when 5 c.c. of M/10-potassium chromate had been added, the pH attained being that required for the precipitation of aluminium hydroxide. At first, the precipitate was white basic aluminium sulphate, but gradually became yellow and contained some chromate (compare Gröger, *Ber.*, 1902, **35**, 3420). The curve shows that very little change in pH ensued until 20 c.c. of potassium chromate had been added. The main inflexion occurred and precipitation became complete when between 32 and 35 c.c. were added. The precipitate was gelatinous and contained chromate, much of which could be removed by washing.

The experiments of Gröger on the solubility of aluminium hydroxide in chromic acid solutions throw some light on the reactivity of the acid. He found that the number of molecules of chromic anhydride required to hold 1 mol. of alumina in solution varied from $4 \cdot 46$ to $5 \cdot 02$, and therefore concluded that both aluminium chromate and dichromate were capable of existence in solution. The explanation lies in the mode of dissociation of chromic acid. The first stage of the ionisation permits of the ready solution of aluminium hydroxide, thus $Al(OH)_3 + 3H_2CrO_4 \rightleftharpoons Al(HCrO_4)_3 + 3H_2O$, which requires 6 mols. of CrO_3 to 1 mol. of Al_2O_3, but the amount of hydrions produced in the second stage of the dissociation

will depend on the concentration of chromic acid used. If it be large, the great concentration of hydrochromate-ions will tend to suppress the second stage of dissociation and consequently there will be proportionally fewer hydrions available for reaction than in a more dilute solution. Hence it is clear why Gröger required variable amounts of chromic acid which corresponded to somewhat less than 6 mols.

Chromium.—Maus (*Pogg. Annalen*, 1827, **9**, 127) and later Storer and Eliot (*Proc. Amer. Acad. Arts Sci.*, 1862, **5**, 192) found that brown precipitates of basic chromium chromate were produced by the action of potassium chromate on solutions of chromium salt, from which the chromic acid could be removed by repeated washing. The latter investigators stated that the abstraction did not stop when the precipitate had attained any particular composition, and, from an equation based on the molecular proportion of potassium chromate which they found necessary for precipitation, concluded that CrO_2 (*i.e.*, $Cr_2O_3 \cdot CrO_3$) must have first been formed.

The titration curve shows that the factor which determined precipitation was the hydrogen-ion concentration, for when 26 c.c. of M/10-potassium chromate had been added and the pH had become 5·2, as compared with 5·34 found for the hydroxide, the basic chromate began to separate. The amount of potassium chromate required was 2·6 mols. to 1 mol. of chromic sulphate, and thus happens to be about half the quantity (5 mols.) found by Storer and Eliot. As the point of precipitation is determined by the hydrion concentration, the amount of potassium chromate required appears to be a function of the concentration of the reactants. The pH change prior to precipitation was indicated by a line which was nearly straight, comparable with the section corresponding to the addition of the first equivalent (to 1 Cr) of sodium hydroxide, in the alkali titration curve (*loc. cit.*). The fact that 2 mols. of sodium hydroxide had to be added to 1 mol. of chromium sulphate before precipitation began was due to the peculiar property of tervalent chromium of forming " soluble basic salts," such that in a solution of the sulphate 1 molecule of sulphuric acid is in a state of loose combination which may perhaps be expressed by the equilibrium $Cr_2(SO_4)_3 + 2H_2O \rightleftharpoons (OH)_2Cr_2(SO_4)_2 \ldots H_2SO_4$, the looseness of the combination being indicated by the dotted line. This molecule of sulphuric acid, on its gradual release, reacted with two molecules of potassium chromate, thus : $H_2SO_4 + 2K_2CrO_4 = 2KHCrO_4 + K_2SO_4$, and the remaining 0·6 mol. of potassium chromate set up an equilibrium with the hydrochromate ions so formed to produce the requisite hydrion concentration for precipitation.

The precipitates formed by treating chromium sulphate solution (as chrome alum) with varying proportions of potassium chromate, corresponding to 30, 60 and 90 c.c. in the titration, were analysed. After being freed from mother-liquor by suction and a little washing by decantation, the first precipitate was green and had the composition, omitting water content, $Cr_2O_3,0\cdot079CrO_3$, and was thus almost pure chromium hydroxide ; the second was brown and contained more chromate, $Cr_2O_3,0\cdot574CrO_3$; and the third, still more, its composition being $Cr_2O_3,0\cdot871CrO_3$.

Beryllium is another of the elements that form soluble basic salts, and this property appears to be reflected in the titration curve, the pH at which precipitation began not being attained until 24 c.c. of $M/10$-potassium chromate had been added, *i.e.*, 1·2 mols. for 1 mol. of beryllium sulphate.

The alkali curve (p. 258) shows a characteristic inflexion during the reaction with the first equivalent of sodium hydroxide ; precipitation occurred at pH 5·69 (given at the top of an inflexion), when 1·04 equivalents had been added. A similar inflexion occurred in the chromate titration curve and precipitation began at pH 5·72, indicated by a point in a similar position. The equivalent amount of potassium chromate which produced this change was 2·4 times that of the alkali and consequently the change in hydrion concentration was due to reaction between a loosely bound equivalent of acid in the beryllium sulphate molecule and potassium chromate, hydrochromate-ions being formed which eventually entered into equilibrium with the added chromate-ions.

Bleyer and Moorman (*Z. anorg. Chem.*, 1912, **76**, 70 ; see also Orlov, *ibid.*, 1913, **79**, 365) found that the interaction of potassium chromate and beryllium sulphate in solution produced very highly basic chromate precipitates, the chromate content of which seemed to increase slightly with the amount of potassium chromate added. Thus with 2 mols. of potassium chromate to one of beryllium sulphate the precipitate contained $BeO,0\cdot036CrO_3$, and with 4 mols. of potassium chromate, $BeO,0\cdot07CrO_3$, some unattacked sulphate being present in each precipitate. Bleyer and Moorman, having found that chromic acid solutions saturated with beryllium hydroxide contained the two in equimolecular proportions, stated that beryllium chromate existed in solution. Solutions of strong acids saturated with beryllia are invariably basic, and, as shown by the titration curve of beryllium sulphate and sodium hydroxide (*loc. cit.*), the solution had to be rendered basic to an extent shown by the formula $Be(SO_4)_{0\cdot5}(OH)$ before precipitation commenced. Similarly, the proportions in Bleyer and Moorman's solutions show

that they were basic to the same extent, *viz.*, $Be(HCrO_4)(OH)$, chromic acid being too weak in its second stage of dissociation to react with beryllium hydroxide to any appreciable extent.

Zinc.—Table 81 shows that the pH of precipitation of basic zinc chromate was 5·49 and therefore a little higher than that of the hydroxide, 5·20. The rapidity with which the pH changed during the addition of the first c.c. of potassium chromate rendered it difficult to ascertain with any degree of precision the exact point at which the precipitate appeared. The precipitate was basic and consequently the hydrion concentration of the solution was controlled mainly by the equilibria between the liberated hydrochromate-ions and chromate-ions. Gröger's analysis (*Monatsh.*, 1904, **25,** 520) showed that the precipitates obtained by treating zinc sulphate solutions with potassium chromate were indefinite and contained some sulphate, but the precipitates obtained from zinc chloride solutions were free from chloride, evidently due to the greater ease with which chlorides are hydrolysed. Varying amounts of potassium chromate were retained but were removable by washing.

An insoluble normal zinc chromate has been stated to exist by Schultze (*Z. anorg. Chem.*, 1895, **10,** 148) and Briggs (*ibid.*, 1908, **56,** 254 ; *J. Chem. Soc.*, 1929, 242). It was thought that, if a difficultly soluble chromate did exist, its solubility might be too large for it to be precipitated by double decomposition through the attainment of the pH at which the basic chromate separated, but that it might be precipitated from a chromic acid solution of zinc oxide by the gradual addition of potassium chromate so that the pH should be kept below that necessary for the precipitation of the basic chromate (compare Britton, *J. Chem. Soc.*, 1924, **125,** 1875). Indefinite basic chromates were always obtained ; *e.g.*, one air-dried precipitate, excluding the water content, corresponded to $ZnO, 0·605CrO_3$, and another corresponded to $ZnO, 0·462CrO_3$.

Gröger (*Z. anorg. Chem.*, 1911, **70,** 135) determined the solubility of zinc oxide in chromic acid solutions varying in concentration from 0·006 M. to 9·7 M. The number of molecules of chromic acid, H_2CrO_4, required to dissolve one molecule of zinc oxide varied continuously with increasing concentration of acid from 1·20 to 2·03, which led Gröger to conclude that the more dilute solutions contained both zinc chromate, $ZnCrO_4$, and zinc dichromate, $ZnCr_2O_7$, whilst the highly concentrated solutions contained only zinc dichromate. The fact that approximately two molecules of chromic acid were required for the most concentrated acid solutions was due to the reaction having taken place between

zinc oxide and the hydrions of the first dissociation, thus : $ZnO + 2H_2CrO_4 \rightarrow Zn(HCrO_4)_2 + H_2O$, the large concentration of hydrochromate-ions having inhibited further ionisation and consequent reaction, whereas in the dilute solutions some of the hydrions from the second stage of ionisation became available for reaction, with the result that less than 2 mols. of chromic acid were required.

Cobalt and Nickel.—Reference may be made to Weil's proposal (*Bull. Soc. chim.*, 1911, **9,** 20) to use potassium chromate for the separation of cobalt from nickel. Although potassium chromate does not precipitate basic nickel chromate at room temperature, the titration curve shows that the hydrion concentration produced by addition of potassium chromate to a nickel salt solution is such that the basic salt is on the point of being precipitated. A method depending on such a small difference in solubility can give but a rough separation, for there will be a great tendency for the gelatinous basic cobalt chromate to carry down much nickel.

Rare Earths.— Yttrium.—Basic yttrium chromate began to be precipitated at the same pH as its hydroxide, but precipitation was far from complete and the precipitate was highly basic. The air-dried precipitate formed by the interaction of stoichiometrical amounts of yttrium chloride and potassium chromate (40 c.c. of $M/10$-K_2CrO_4 in the titration) solutions contained the formula $Y_2O_3,1\cdot30CrO_3$. The filtrate from this precipitate was treated with more potassium chromate, and the new precipitate was still more basic and contained $Y_2O_3,0\cdot93CrO_3$.

Neodymium and Samarium.—These two elements form well-defined but comparatively insoluble chromates (Britton, *J. Chem. Soc.*, 1924, **125,** 1875) ; the power of these earths to unite with chromic acid in its two stages being, no doubt, due to the small solubility of the salts formed, rather than to the strength of the bases. The solubilities of praseodymium chromate and lanthanum chromate are so small that when potassium chromate is added to the respective salt solutions the conditions requisite for the precipitation of the normal chromates are obtained before the hydroxide pH is reached. This is not so with neodymium and samarium chromates, for they are sufficiently soluble to allow the pH at which the hydroxide is precipitated to be attained before the respective solubility products of the chromates are exceeded, and consequently basic chromate precipitates are produced. When neodymium nitrate solution was treated with potassium chromate, a flocculent precipitate was obtained which on microscopic examination was seen to contain crystalline needles similar

to those of the normal chromate. The following precipitates were so obtained: (1) $Nd_2O_3,2\cdot64CrO_3, 9\cdot02H_2O$, and (2) $Nd_2O_3,2\cdot23CrO_3,7\cdot88H_2O$. The fact that precipitation began at pH 6·48 instead of at 7·0, coupled with the nature of the precipitates and the relatively high CrO_3 content, indicates that the formation of these precipitates constitutes a comparatively rare example of the co-precipitation of the crystalline normal salt and an indefinite basic salt.

Samarium chromate has a greater solubility than neodymium chromate and does not appear to be precipitated with the basic chromate. As the titration curve shows, the basic chromate was precipitated at pH 6·55, which was somewhat lower than the hydroxide pH. It was yellow and flocculent and when dried and examined under the microscope appeared to be entirely amorphous. Its separation was partial. The air-dried precipitate from the titration contained 25·1 per cent. CrO_3 as compared with 37·84 per cent. in $Sa_2(CrO_4)_3,8H_2O$.

II. Basic Borates.

Electrometric titrations were carried out at 18° with 0·05 M.-borax solution and salt solutions, which were so chosen that the precipitation reactions could be studied over as wide a range of hydrogen-ion concentration as possible. Details of the solutions used and the pH's at which precipitates first appeared are in Table 82.

TABLE 82.

PRECIPITATION OF BASIC BORATES.

Solution (100 c.c.).	Precipitation of Basic Borate began:		Precipitation of Hydroxide began:		Precipitation.
	E.M.F.	pH.	E.M.F.	pH.	
0·01 M.-ZrCl₄	0·517	4·07	0·390	1·86	Complete
0·01 M.-ThCl₄	0·554	4·70	0·484	3·51	,,
0·0067 M.-Al₂(SO₄)₃	0·521	·4·14	0·521	4·14	,,
0·01 M.-Cr₂(SO₄)₃,K₂SO₄	0·586	5·25	0·591	5·34	,,
0·02 M.-BeSO₄	0·613	5·72	0·610	5·69	,,
0·02 M.-ZnSO₄	0·587	5·27	0·583	5·20	,,
0·02 M.-MnCl₂	0·792	8·82	0·770*	8·43*	Partial
0·02 ,,	—	—	0·794	8·85	
0·02 M.-MgSO₄	—	—	0·885	10·49	None

The titration curves are given in Fig. 70, the arrows showing the points at which precipitation began. The top curve in the diagram

represents the titration of 100 c.c. of 0·02 M.-manganous chloride
with 0·1018 M.-sodium metaborate.

Table 82 shows that, except in the case of zirconium and
thorium, addition of borax solution did not cause precipitation
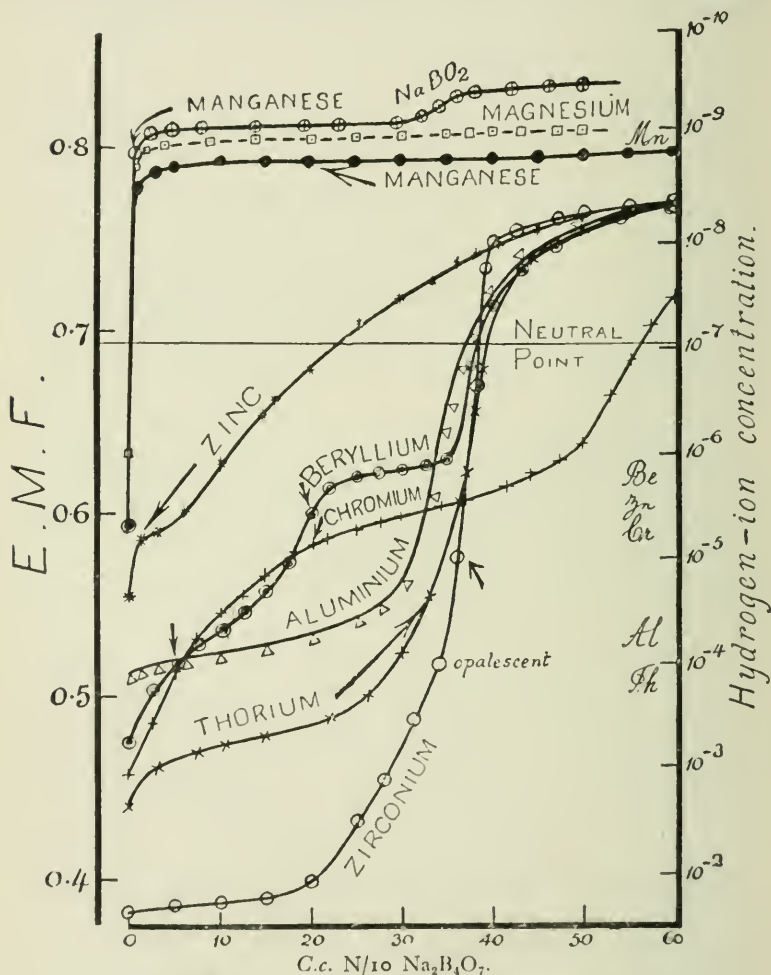
FIG. 70.—Precipitation of Basic Borates.

to begin until the pH at which the hydroxide is precipitated had
been attained. The titration curves in Fig. 70, apart from that of
zinc, are similar in shape to those representing the alkali titrations.
Moreover, those curves which correspond to precipitation taking
place in the acid zone show that the amounts of N/10-borax

solution which caused the solutions to become alkaline, precipitation having become complete, were approximately the same as those required in the sodium hydroxide titrations. It appears, therefore, as far as the weaker bases are concerned, that sodium pyroborate has simply a hydrolysing action in precipitating the hydroxides, and in fact behaves as if no borate were present at all. The hydroxides which were precipitated contained some unattacked acid radical of the original salt, as may be seen from the amounts of N/10-borax required to render the solutions neutral, if it be assumed that the borate radical did not enter into combination. Thus in the zirconium titration, 38·5 c.c. were required as compared with the theoretical amount, 40 c.c. ; thorium, 38·0 instead of 40 c.c. ; aluminium, 36·0 instead of 40 ; chromium, 55 instead of 60 ; and beryllium, 37·6 instead of 40 c.c.

Provided that no insoluble normal borates are formed, it follows on theoretical grounds that boric acid, HBO_2, with its exceptionally small dissociation constant, is incapable of producing hydrogen-ion concentrations large enough to cause dissolution of any of the hydroxides which are precipitated at pH less than 7. Boric acid behaves as a monobasic acid. If 5×10^{-10} be taken as an average value of $K = [H^{\cdot}][BO_2']/[HBO_2]$, it follows that in a M/10-boric acid solution the hydrogen-ion concentration is $10^{-5·2}$, and $10^{-5·6}$ in a M/100-solution. The hydroxides of beryllium, zinc, chromium, aluminium, thorium, and zirconium are all precipitated at pH values equal to, or less than 5·69, and consequently the hydrion concentrations of M/10- and M/10-solutions of boric acid are too small to have any solution effect on these hydroxides. Taking the case of beryllium hydroxide, which is precipitated at the highest pH of the series under consideration, in order that the reaction $Be(OH)_2 + 2HBO_2 \rightleftharpoons Be(BO_2)_2 + H_2O$ may proceed, water must be formed and therefore the product of the concentration of hydroxyl ions due to beryllium hydroxide, $viz.$, $10^{-14·14}/10^{-5·69} = 10^{-8·45}$, and that of the hydrions from the boric acid, about $10^{-5·2}$, must exceed K_w. In this case it is $10^{-13·9}$, and only just exceeds K_w, and consequently beryllium hydroxide may perhaps be expected to exhibit the slightest tendency to dissolve. Any dissolution, however, would cause an increase in the concentration of BO_2' ions, which would depress the ionisation of boric acid and so prevent further solution. Boric acid does not dissolve either of these bases to any perceptible extent.

The hydrogen-ion concentrations of the solutions at the end of these titrations are such as would be given by borate mixtures comprising the total quantity of boric acid added and the alkali in excess of that required for the precipitations, and therefore confirm

the view that no boric acid, or relatively little, was contained in the precipitates. Thus in the titrations of zinc, beryllium, aluminium, thorium, and zirconium, it will be seen from Fig. 70 that the hydrion concentration when 60 c.c. of $N/10$-borax had been added was $10^{-8.3}$ in each case. By subtracting the 40 c.c. of $N/10$-sodium hydroxide which were neutralised during the precipitations, it is found that the solutions contained alkali equal to 20 c.c. of $N/10$-sodium hydroxide and boric acid equal to 120 c.c. of $N/10$-HBO_2, the boric acid having been one-sixth neutralised. The pH of a 0·2 N-solution of boric acid neutralised to the same extent is, according to Sϕrensen, 8·29 (p. 185), and as the variation in pH produced by the difference in concentration of the two solutions is very small, it will be seen that the agreement is sufficiently good.

Although the changes in hydrion concentration which took place in the acid zone of the titrations are almost identical with those which were obtained when the precipitant was sodium hydroxide, in the case of the two weakest bases, zirconia and thoria, the pH's of precipitation do not compare favourably with the corresponding hydroxide pH's. Zirconium hydroxide is generally precipitated at a pH somewhere on the very slightly inclined part of the curve. In the precipitation of zirconium chloride solution with sodium hydroxide (p. 263) the pH was 1·86, but in the present titration the solution remained perfectly clear until the inflexion in the curve had been passed and the pH had become 4·06 ; opalescence then began. This was when 3·4 atoms of chloride of the zirconium tetrachloride had been replaced by hydroxyl groups and, notwithstanding its highly basic nature, the solution had remained perfectly clear. With thorium chloride the effect was similar ; the solution remained quite clear until 3·3 atoms of chloride had been replaced and the curve had begun to incline, the pH being 4·70 instead of 3·51 obtained by using alkali. Hence it appears that the boric acid was having some restrictive influence on the growth of the particles. It is probable that the tendency, although very slight, which boric acid may have to combine with thoria and zirconia exerts its greatest influence just at the point where the hydroxide or basic salt is about to pass into colloidal solution prior to precipitation. If this be the case, it seems reasonable that the boric acid, in trying to react with the nascent hydroxide, tended to keep it in solution by impeding the growth of the particles. Two experiments were made to determine whether the delayed precipitation from a thorium chloride solution whose pH is that at which precipitation normally takes place is a matter of time. To thorium chloride solutions of the concentration used in the

titration were added amounts of borax equal to 2 and 3 equivalents ; in neither case did a precipitate separate during a period of several weeks.

In the chromium titration the solution became green on addition of the borax and precipitation occurred when 21·9 c.c. of N/10-solution had been added, or 1·09 equivalents for each atom of chromium.

The beryllium curve again is similar to the alkali curve, and precipitation was also delayed until 21·9 c.c. (= 1·09 equivalents to 1 atom of Be) had been added.

The zinc curve shows hydrogen-ion changes which were due mainly to equilibria which must have been set up between borate ions and boric acid. The precipitation pH was the same as that when alkali was used.

The incomplete precipitation which took place from M/50-manganous chloride solution will be understood when it is remembered that the pH of N/10-borax itself, $viz.$, 9·11, is only slightly greater than the pH at which manganous hydroxide is precipitated. Table 82 gives two pH values for manganous hydroxide ; the one marked with an asterisk is low, probably on account of oxidation of manganous hydroxide, and the other, which is approximately correct, was extrapolated from the alkali titration curve. In the borax titration the precipitate did not appear until 20 c.c. of N/10-borax had been added and pH 8·82 attained. The precipitate was white and remained dispersed until 50 c.c. had been added, but, unlike the hydroxide, it did not immediately turn brown through oxidation. It readily did so when washed. (It is this protective action which is conferred on manganous hydroxide by union with some boric acid which makes the substance of use as a " drier " in paints and varnishes.) The fact that it was precipitated at the hydroxide pH suggests that the white precipitate was basic, and not manganous borate as was stated by Hartley and Ramage ($J.$ $Chem.$ $Soc.$, 1893, **63**, 133). The precipitate produced by the action of N/10-borax on M/50-manganous chloride solution was both indefinite and basic and contained $MnO,1·47HBO_2$. In the titration of M/50-manganous chloride with 0·1018 N-sodium metaborate, the precipitate appeared when 1 c.c. of precipitant had been added and the pH had become 8·77. This precipitate was, like the hydroxide, quickly oxidised and was strongly basic.

Laurent ($Comp.$ $rend.$ $Trav.$ $Chim.$, 1850, **6**, 33) observed that manganous salt solutions were not precipitated with potassium hexaborate. It will be seen from the hydrogen-ion concentrations of the various " buffer " mixtures that the pH of a boric acid solution, a third of which has been neutralised with alkali and

which thus corresponds to Laurent's reagent, is about pH 8·7, which just falls below the pH at which the hydroxide is precipitated. When, however, the borate solution is added to a manganous salt solution, some of the alkali is neutralised and the pH falls a little further below 8·7.

According to Gmelin-Kraut (*Handbuch anorg. Chem.*, 1908, iii, [2], p. 324), Berzelius found that when a magnesium salt had been added to a manganous salt solution, borax failed to give a precipitate. Neutral salts, such as sodium chloride, sodium sulphate, calcium chloride and potassium chloride, also produce this effect, but to a lesser extent ; *e.g.*, a solution from which precipitation had been prevented with magnesium sulphate remained clear on standing, whereas by using either potassium chloride or any of the other salts brown precipitates appeared after 12 hours. Precipitates obtained by means of borax may be forced back into solution by the addition of these salts. Since the highest pH that could be produced by borax solutions was far removed from the precipitation pH of manganous hydroxide, it appeared that the behaviour of these salts in preventing precipitation of basic manganous borate lay in their power to diminish the pH below that necessary for precipitation. For example, when 10 c.c. of a saturated solution of magnesium sulphate were added to 100 c.c. of $N/10$-borax solution whose initial pH was 9·11, the pH fell to 8·58 ; with 40 c.c., pH was 8·10 ; and with 50 c.c., 8·06. The effect of potassium chloride was not so marked. The addition of much potassium chloride to a $N/10$-borax solution depressed the pH only from 9·11 to 8·82—a value, it will be noticed, corresponding to incipient precipitation.

The dotted curve shows the changes produced in hydrogen-ion concentration during the addition of $N/10$-borax solution to a $M/50$-solution of magnesium sulphate. No precipitate was obtained, for the pH of the borax solution was below that, 10·49, requisite for the precipitation of magnesium hydroxide. Borax produces in the boiling solution a precipitate which redissolves on cooling. No precipitate was obtained with $N/10$-sodium metaborate solution, for although its pH was 10·85, the pH of the mixture became a little lower than the necessary value.

III. Basic Carbonates.

The hydrogen electrode titration method has been applied in a study of the relationships involved in the precipitation of basic carbonates. By using a plentiful supply of hydrogen in electrodes which were efficient in ordinary solutions, potential differences

between them and the normal calomel electrode were obtained, in these carbonate titrations, which were readily reproducible and were unaffected by any liberated carbon dioxide. Table 83 gives
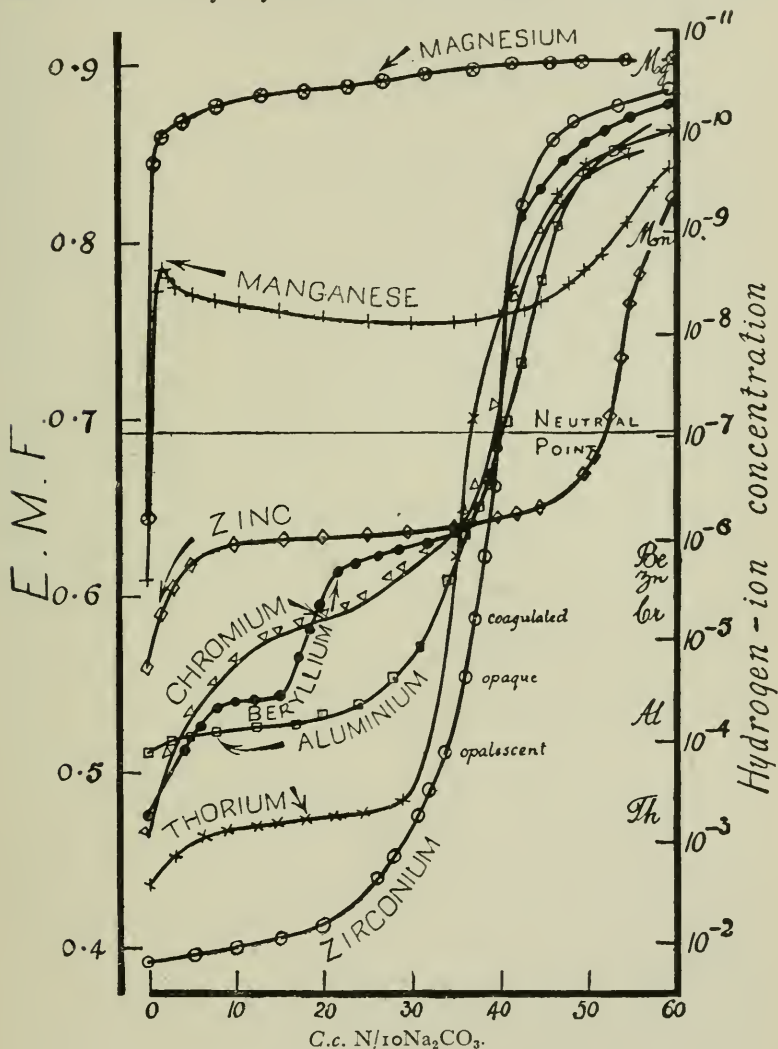
FIG. 71.—Precipitation of Basic Carbonates.

the particulars of the several titrations, and Fig. 71 shows the titration curves, the points at which precipitation began being again denoted by arrows. The sodium carbonate was decinormal in every case except in the chromium titration, when it was 0·166 N.

TABLE 83.
PRECIPITATION OF BASIC CARBONATES.

Solution (100 c.c.).	Precipitation of Basic Carbonate began:		Precipitation of Hydroxide began:		Precipitation.
	E.M.F.	pH.	E.M.F.	pH.	
0·01 M.-$ZrCl_1$	0·511	3·95	0·390	1·86	Complete
0·01 M.-$ThCl_4$	0·476	3·35	0·484	3·51	,,
0·0067 M.-$Al_2(SO_4)_3$	0·523	4·16	0·521	4·14	,,
0·01 M.-$Cr_2(SO_4)_3,K_2SO_4$	0·587	5·27	0·591	5·34	,,
0·02 M.-$BeSO_4$	0·612	5·70	0·610	5·69	,,
0·02 M.-$ZnSO_4$	0·589	5·30	0·583	5·20	,,
0·02 M.-$MnCl_2$	0·784	8·68	0·794	8·85	,,
0·02 M.-$MgSO_4$	0·891	10·54	0·885	10·49	Turbidity

The titration curves are of the same type as those obtained in the preceding hydrolytic precipitation titrations, and in every case but zirconium, precipitation began at hydrion concentrations equal or very nearly equal to those necessary for the corresponding hydroxides. N/10-sodium carbonate, unlike the reagents used in the previous titrations, when added to the magnesium sulphate solution, produced an alkalinity corresponding, but only just so, to the pH at which the hydroxide is precipitated, which did not occur until 27 c.c. had been added. The precipitate formed even after 100 c.c. of sodium carbonate had been added did not amount to more than a slight turbidity.

The stoichiometrical quantity of sodium carbonate required for simple double decomposition was equivalent to 40 c.c. of N/10-sodium carbonate, except in the case of chromium, where it was 36 c.c. The curves for zirconium, thorium, aluminium, beryllium, and chromium show that the mother-liquors became alkaline when approximately theoretical quantities of sodium carbonate had been added. The hydrion concentrations at the end of the titrations, although differing somewhat owing to the escape of different amounts of carbon dioxide during the precipitations, were such as would be produced by mixtures of sodium bicarbonate and carbonate (compare Prideaux, *Theory of Indicators*, p. 299 ; Auerbach and Pick, *Arb. K. Gesundheitsamt.*, 1911, **38**, 243). The changes in hydrion concentration which took place during the precipitation of the basic carbonates from solutions whose hydrogen-ion concentrations were greater than 10^{-6} were scarcely at all affected by the carbon dioxide that was liberated. The carbon dioxide set free during the precipitation of basic zinc carbonate, however, had so marked an effect on the hydrogen-ion concentration that the inflexion corresponding to the formation of sodium

bicarbonate from the liberated carbon dioxide and the added sodium carbonate did not occur until 54 c.c. of the latter had been added.

The curve for manganese shows that the addition of $N/10$-sodium carbonate, after the first 2 c.c., produced a diminution in pH, which reached a minimum at pH 8·2 when 30 c.c. had been added. The precipitate appeared when 1·4 c.c. had been added and pH 8·68, *i.e.*, nearly the hydroxide pH, had been attained. The precipitate first formed was basic, as may be seen from the curve, which shows that more than 40 c.c. of sodium carbonate had to be added before the pH of sodium bicarbonate was attained, *viz.*, 8·7.* The precipitate, although basic, did not turn brown through oxidation by the air. It is remarkable that the increase in hydrion concentration which occurred during the titration did not cause the basic carbonate to re-dissolve. This, however, was a case of two precipitations, one of the basic carbonate due to the pH's ruling at the beginning and at the end of the reaction, and the other of the normal carbonate, which was precipitated when the hydrion concentration of the solution was enhanced. Sodium bicarbonate when added to a manganous chloride solution, preferably saturated with carbon dioxide, causes the precipitation of manganous carbonate only, for it cannot produce a sufficiently low hydrion concentration to enable the basic carbonate to separate from solution ; *e.g.*, the hydrion concentration of a manganous chloride solution was gradually reduced by the addition of a solution of sodium bicarbonate until the pH was 7·6, when a white precipitate of manganous carbonate began to form. Hence, in order to ensure the precipitation of the normal carbonate, the precipitant must be incapable of causing the pH to be attained at which the hydroxide is precipitated.

Normal zinc carbonate has been prepared. The titration curve shows that in order to precipitate this salt uncontaminated with basic carbonate a reagent must be used which, besides causing the solubility product $[Zn^{\cdot\cdot}][CO_3'']$ to be exceeded, will maintain a hydrogen-ion concentration greater than that at which the basic carbonate would separate. Sodium bicarbonate with its pH of 8·7 would be useless, even though the carbon dioxide which would be set free during the precipitation would tend to increase the hydrion concentration. It would be necessary to have the solution saturated with carbon dioxide under a very high pressure before any addition of sodium bicarbonate. Smith (*J. Amer. Chem. Soc.*,

* It may be calculated from Noyes's formula (*Z. physikal. Chem.*, 1893, II, 495), by taking K_1 and K_2 of carbonic acid to be 3×10^{-7} and K_2 $1\cdot3 \times 10^{-11}$, respectively, that the pH of dilute solutions of sodium bicarbonate is about 8·7.

1918, **40**, 883) has determined the solubility of zinc carbonate in solutions of carbon dioxide under pressures ranging from 4·12 to 40·6 atmospheres. His results may be used to calculate the hydrogen-ion concentrations of the various solutions which, being in equilibrium with zinc carbonate, were just on the point of precipitating zinc carbonate, if it be assumed, as was done by Bodländer (*Z. physikal. Chem.*, 1900, **35**, 23), that metallic bases exist in carbonic acid solutions in the form of bicarbonates. If zinc oxide exists as $Zn(HCO_3)_2$, the concentration of HCO_3' ions is equal to twice the concentration of dissolved zinc oxide, and, the extremely small concentration of hydrions arising from carbonic acid in its second stage of dissociation being neglected, it follows that $[H^·] = [H_2CO_3]K_1/[HCO_3'] = ([CO_2] - 2[ZnO]) \cdot 3 \times 10^{-7}/2[ZnO]$. It was thus calculated that the pH's of Smith's solutions varied continuously from 4·94 to 4·33. Even when the pressure of carbon dioxide is very high, the pH at which the normal carbonate is precipitated is not very much less than that at which the hydroxide is precipitated.

Mikusch (*Z. anorg. Chem.*, 1908, **56**, 365) determined the solubility of zinc oxide in carbon dioxide solutions in equilibrium with basic zinc carbonate. By means of the above formula, it was found that the pH's of his solutions lay between 6·05 and 6·15. These hydrion concentrations, though somewhat higher than that at which basic zinc carbonate began to separate in the present titration, *viz.*, pH 5·3, happen to be those that obtained during the main course of the precipitation. As zinc carbonate exists in equilibrium with hydrogen-ions at a relatively high concentration, it follows that water will decompose zinc carbonate to give the less soluble basic carbonate.

The hydrogen-ion concentration which had to be attained in the magnesium titration before sodium carbonate produced a precipitate shows that, contrary to the statements of several workers, the precipitate was basic. The solubility product of magnesium carbonate, $MgCO_3,3H_2O$, at 18° is $1·2 \times 10^{-4}$ (Johnston, *J. Amer. Chem. Soc.*, 1915, **37**, 2014), and consequently, if complete dissociation be assumed, the solubility of magnesium carbonate is $1·1 \times 10^{-2}$ mol. per litre. The solubility of magnesium hydroxide, obtained from the solubility product, 2×10^{-11}, is $2·7 \times 10^{-4}$ mol. per litre. Hence, to precipitate the more soluble magnesium carbonate, a precipitant must be used which will supply the necessary carbonate-ions without introducing the concentration of hydroxyl-ions that causes the separation of magnesium hydroxide. As magnesium hydroxide is precipitated at pH 10·5, it is obvious that sodium bicarbonate (pH 8·7), even

although added in large excess, cannot produce the corresponding concentration of hydrogen-ions, and therefore cannot precipitate basic magnesium carbonate. It can, however, supply the carbonate-ions which, provided that the magnesium salt solution is sufficiently concentrated, will cause magnesium carbonate to separate. Boussingault (*Ann. Chim. Phys.*, 1825, **29,** 285) found that sodium sesquicarbonate, $Na_2CO_3,2NaHCO_3$, also could be used for this purpose. The data of Auerbach and Pick (*loc. cit.*) show that the pH of such a mixture, decinormal with respect to carbonic acid, is approximately 9·9, which is just a little below the value required for the precipitation of the hydroxide.

No normal carbonates of chromium, beryllium, aluminium, thorium, and zirconium are known, and, as would be expected, the precipitates they form are highly basic. The shape of the beryllium titration curve appears to be peculiar to that element, and the precipitate did not appear until 22 c.c. (= 1·1 equivs. Na_2CO_3 to 1 mol. $BeSO_4$) of sodium carbonate had been added. In the chromium and thorium titrations, precipitation did not begin until 20 c.c. (1·85 equivs. to 1 Cr) and 18 c.c. (1·8 equivs.), respectively, of sodium carbonate had been added. As may be seen from Table 83, the precipitation which took place from thorium chloride solution with sodium carbonate was due to the attainment of the pH at which the hydroxide is precipitated and therefore the precipitate was basic. Chauvenet (*Comp. rend.*, 1911, **153,** 66), having found that the analysis of such a precipitate corresponded to the formula $ThO_2,CO_2,8H_2O$, stated that it was normal thorium orthocarbonate, $ThCO_4, 8H_2O$, a salt of a purely hypothetical acid. In the case of the zirconium titration the curious effect noted in the borate titration was again observed, opalescence not beginning until 3·4 equivalents of sodium carbonate had been added and the relatively high pH of 3·95 had been attained. In the borate titration the pH was 4·06, and 3·4 equivalents of borax were required. As mentioned above, this phenomenon is believed to be due to suppression of the growth of the basic particles owing to a slight solvent action of the liberated weak acid.

IV. Basic Silicates.

Attention was (*J. Chem. Soc.*, 1927, 425) directed to the action of solutions of sodium silicate on typical metallic salt solutions. The precipitates thus obtained have received comparatively little attention, and the very few formulæ which have been assigned to them show that the ratio of silica to base is always higher than that required to form the metasilicate. Some investigators have, however, mentioned that their precipitates contained free silica. The

difficulties inherent in the separation of a silicate precipitate, often containing free silica, from its mother-liquor in anything approximating to the pure state (of which there is usually no criterion), are so great that it is probable that the few analyses which have been made convey no idea of the reaction which took place. We see from the curve on page 414 that the acidic property of silicic acid asserts itself only in alkaline solutions, and consequently it would be expected that very little action could take place between it and those hydroxides which are precipitated from acid solutions, unless the substances formed by the interaction are extremely insoluble. The view has been advanced, however, to account for the acidity of " soil solutions," that complex aluminosilicic acids exist in the soil through the interaction of aluminium hydroxide and silica. If any such combination could take place, it is probable that it would have some effect on the hydrogen-ion concentration of the mother-liquor. It was therefore decided to investigate electrometrically the changes in hydrogen-ion concentration when solutions of sodium silicate and of metallic salts are allowed to interact. The sodium silicate employed was prepared from water-glass containing 2·16 mols. SiO_2 to 1 mol. Na_2O, and was 0·1020 N with respect to sodium hydroxide. The impurities therein, including carbon dioxide, were so small as to have no measurable effect on the E.M.F. measurements. The solutions used are given in Table 84, together with the pH at which precipitation began, the

TABLE 84.

PRECIPITATION OF SILICATES.

Solution Titrated (100 c.c.).	Precipitation began at—		Hydroxide Precipitation at pH.
	pH.	C.c. of Sodium Silicate.	
0·01 M.-ZrCl₄	3·98	35·0	1·86
0·01 M.-ThCl₄	3·50	30·0	3·51
0·0067 M.-Al₂(SO₄)₃	4·04	5·0	4·14
0·02 M.-BeSO₄	5·31	20·0	5·69
0·02 M.-ZnSO₄	5·25	1·0	5·20
0·02 M.-MnCl₂	7·35	1·0	8·41
0·02 M.-MgSO₄	9·50	1·0	10·49
0·02 M.-CaCl₂	10·07	3·0	—

amount of reactant which had to be added, and the pH at which the respective hydroxides are precipitated.

The titration curves are plotted in Fig. 72, in which the beginning of precipitation is marked by arrows. The amount of sodium silicate required in each reaction such that the alkali was in a quantity equivalent to the acid radical in 100 c.c. of salt solution

was 39 c.c. The curves lying beyond 39 c.c. illustrate the effect of increasing amounts of sodium silicate on the hydrogen-ion concentration of the mother-liquor. The equation

$$Na_2O,2\cdot16SiO_2 + RCl_2 \rightarrow 2NaCl + RO,xSIO_2 \downarrow + (2\cdot16 - x)SiO_2$$
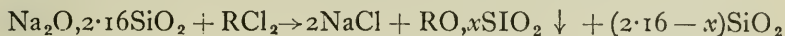
shows that after the silicate $RO,xSiO_2$ had been precipitated by the 39 c.c., the mother-liquor comprised a sodium salt (chloride or sulphate), which through its very small concentration would have no measurable effect on the P.D., and a certain amount of silicic acid which had escaped precipitation and would exert a buffering
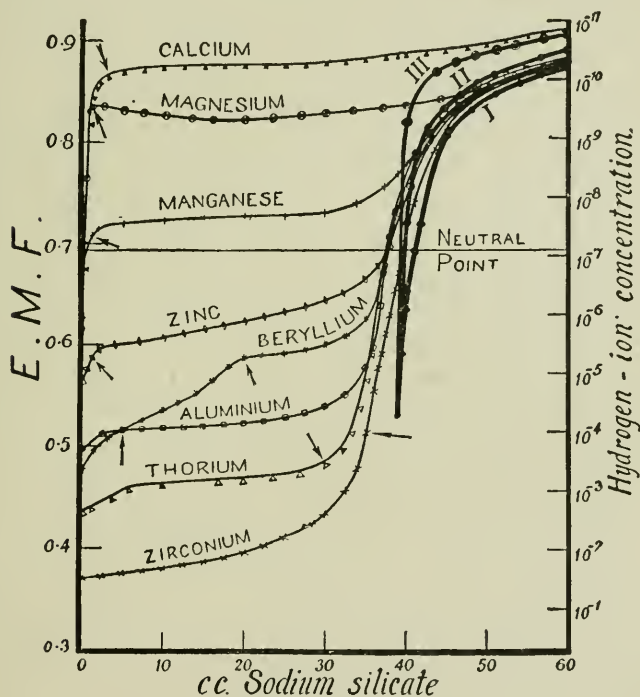
FIG. 72.—Precipitation of Basic Silicates.

effect on the excess of sodium silicate. Some measure of the amounts of the silica which had remained in solution, and therefore of the amounts which had been precipitated with the metallic hydroxides, was obtained by following the changes in hydrogen-ion concentration when sodium silicate, of the same concentration as that used for the precipitations, was added to solutions having the volume attained when the precipitations had become complete, *viz.*, 139 c.c., and containing the same concentration of neutral sodium

salt as the original mother-liquors but different amounts of silica. Thus Curve I (Fig. 72) represents the course taken when sodium silicate was added to 139 c.c. of solution containing 39 c.c. of sodium silicate exactly neutralised (to methyl-orange) with hydrochloric acid ; it would therefore have been the curve obtained if the hydroxides alone had been precipitated and all the silica had remained in solution. Curve II shows the variation in hydrogen-ion concentration which would have been produced if the metasilicates of the metals had been precipitated, and the remainder of the silica had been left in solution ; whereas Curve III corresponds to the change which would have occurred if all the silica present in the 39 c.c. had been precipitated. Except for the calcium curve, those sections of the curves corresponding to an excess of sodium silicate lie between Curves I and II. Hence the amounts of silica carried down with the various precipitates were somewhat smaller than that necessary for the formation of normal metasilicates. Table 84 shows that the pH's at which the silicate precipitates of thorium, aluminium, and zinc separated were also those at which the respective hydroxides begin to be precipitated. In the case of the zirconium titration, the silicate precipitate did not appear until pH 3·98 was reached, as compared with pH 1·86 for the hydroxide when precipitated from chloride solution. The curve in the acid zone shows that the change in hydrogen-ion concentration was similar to that which occurred in the precipitations of the hydroxide, basic borate, and basic carbonate. Precipitation was delayed until 3·59 equivs. of alkali had been added, whereas in the hydroxide precipitation opalescence appeared with 1·5 equivs. Delayed precipitation was also noted with the basic borate and carbonate—3·4 equivs. of reactant being required in each case, and the pH's being 4·07 and 3·95, respectively. It is remarkable that the silica in the reagent should have impeded the precipitation until an almost identical pH, 3·98, had been attained. The other precipitate formed whilst the mother-liquor was still acidic was that of beryllium ; this began to form at pH 5·31, which is slightly lower than the hydroxide pH, 5·69. As in previous work with beryllium, the precipitate did not begin to form until 1·01 equivs. of alkali, as sodium silicate, had been added. The difference between the two pH's may be due to the fact that the silicic acid formed in the course of the reaction became very unstable on approaching the neutral point. The pH's at which the magnesium and manganese precipitates began to form are considerably less than those of the respective hydroxides. The cause probably lies in the insolubility of silicic acid, which cannot therefore retain a base in solution until the

hydroxide pH is reached. This is not the case with those pre-
cipitates which are formed in acid solutions, for then the acid
liberated by the hydrolysis of the salts is sufficient to maintain
solution until the corresponding hydroxide pH is attained, or
nearly so. The interaction of sodium silicate and a solution of
calcium chloride produced a curve which shows that when the
stoichiometrical amount of alkali, as silicate, had been added,
the alkalinity of the mother-liquor was greater than that which
would have been sent up if all the silica in the sodium silicate had
been removed from solution by the calcium precipitate and an
excess of alkali had been added instead of sodium silicate. In the
other reactions investigated, it is probable that, owing to the great
weakness of silicic acid, very little or no combination took place
between it and the various hydroxides, the silica in the precipitates
having been the result of simultaneous precipitations. It is
nevertheless surprising that all the silica attached to those portions
of the reagents which were responsible for the precipitations was
not itself completely precipitated with the hydroxides. It is, of
course, possible that the excess of sodium silicate which was
subsequently added peptised some of the silica which had origi-
nally been precipitated. The formation of silicate precipitates
is probably the result of the mutual coagulation of oppositely
charged colloids through the removal by neutralisation of the
substances which tended to stabilise or to peptise them, as found
by Thomas and Johnston (*J. Amer. Chem. Soc.*, 1923, **45**, 2532)
in the case of the mutual coagulation of a ferric hydrosol, peptised
by ferric chloride, and a silica sol, peptised by sodium silicate.

The precipitation of calcium silicate is, however, of quite a
different nature in that calcium hydroxide is fairly soluble in water
and is, moreover, sufficiently strong a base to react with silicic
acid. The alkalinity of the solution was caused by the considerable
hydrolysis of the calcium silicate, and the exceptionally high pH
of the solution after 39 c.c. of sodium silicate had been added was
apparently due to the withdrawal by the precipitate of more silica
from the reagent, the precipitate thus containing more than 2 mols.
of SiO_2 to 1 mol. of CaO.

In order to study the reactions (and consequent precipitations)
between silicic acid and the alkaline earths, hydrogen-electrode
titrations were carried out at 18° of solutions of 100 c.c. of 0·01112
M.-SiO_2 with each of the following solutions : 0·0447 N-calcium
hydroxide, 0·0558 N-barium hydroxide, and 0·0359 N-strontium
hydroxide. The solutions were prepared immediately before
the titrations by neutralising sodium silicate solutions with hydro-
chloric acid, using methyl-orange, in order that they should

contain the acid in a condition of maximum reactivity and that any diminution by ageing or by precipitation of the silicic acid should be avoided. These very dilute solutions though colloidal were quite clear. The titration curves given in Fig. 73 show that precipitation of the silicates did not begin until appreciable amounts of alkaline-earth solutions had been added, and when approximately the same hydrogen-ion concentrations had been attained. Thus the compositions of the solutes when on the point of precipitation were $CaO,5 \cdot oSiO_2$; $BaO,5 \cdot o7SiO_2$; and $SrO,5 \cdot 54SiO_2$; the respective pH's being $9 \cdot 74$, $9 \cdot 72$, and $9 \cdot 90$. In the case of the calcium and barium titrations marked inflexions occur between pH 10 and 11, but in the strontium titration an inflexion is scarcely perceptible. It was found that, in the calcium and barium reactions, these inflexions denoted the points when the silica and the whole of the added alkaline earths had become precipitated; hence the precipitates must have been $CaO,3 \cdot o2SiO_2,xH_2O$ and $BaO,2 \cdot 85SiO_2,xH_2O$.
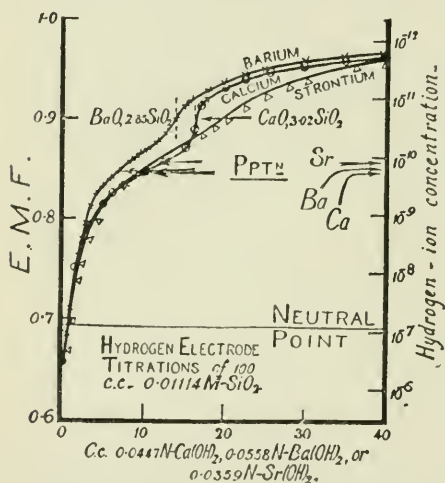
FIG. 73.—Precipitation of Alkaline Earth Silicates.

The hydrogen-ion concentrations of the solutions thereafter indicate that some further reaction took place between the precipitates and the added alkaline-earth solutions. The hydrogen-ion concentrations of the solutions prior to precipitation are comparable with those produced with sodium hydroxide (*vide* Fig. 91), showing that the condition in which the silicic acid is present in both the alkali and the alkaline-earth solutions is similar. It seems reasonable to suppose that the high proportion of silica retained in the solutions must be due to some colloidal micellar formation.

The amounts of silica found in " soil solutions " at any pH value are very small even when their calcium contents are comparatively high. This seems to be contrary to what might be expected from the foregoing observations. The absorption of carbon dioxide,

however, is sufficient to decompose any calcium silicate solutions which may be formed.

The absorption of alkaline earths by silica gel suspended in water was marked by a slow and gradual diminution in hydrogen-ion concentration. The curves showed a "buffer action," the extent of which depended on the amount of silica employed, commencing from pH 6·5, instead of the sharp change shown in Fig. 73, where the silica was not in great excess. The buffer action of the silica gel is comparable with that which takes place when slaked lime is added to a soil, the reaction being usually between pH 6·5 and 9.

The action of alkalis and alkaline earths on aluminium hydroxide in forming soluble aluminates whose solutions are appreciably alkaline in reaction (see Figs. 62 and 63), coupled with the action of alkalis and alkaline earths on silicic acid afford an explanation of the formation of permutites and zeolites. The compositions of most of the zeolites may be expressed by the general formula $RO,Al_2O_3,xSiO_2,yH_2O$, where R may represent one atom of a bivalent metal or two of a univalent metal, and $x =$ or > 2. For Gans's synthetic permutites x varied from 3 to 4. They were prepared by the action of alkali-metal aluminate solutions on silicic acid, and not by the action of alkali-metal silicate on aluminium hydroxide. It has been shown that the amounts of alkali or alkaline earth which dissolve aluminium hydroxide to form the soluble aluminate are approximately the same as those indicated by the formula R^IAlO_2, $viz.$, either 1 mol. R^I_2O or 1 mol. $R^{II}O$ to 1 mol. Al_2O_3. This happens to be the ratio found in zeolites. Calcium aluminate solution on reacting with silicic acid, as either sol or gel, decomposes between pH 7 and 9 to give precipitates of calcium silicate (indefinite) and aluminium hydroxide, the aggregate composition of the precipitates being

$$CaO,Al_2O_3,xSiO_2,yH_2O.$$
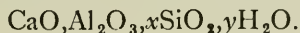
CHAPTER XVII.

DEPENDENCE ON HYDROGEN-ION CONCENTRATION OF THE REACTIONS BETWEEN SOLUTIONS OF SALTS OF HYDROXIDES OF LOW PRECIPITATION pH AND THE SODIUM SALTS OF WEAK ORGANIC ACIDS.

HITHERTO we have been concerned with reactions between certain metallic salts and alkali-metal salts of very weak inorganic acids (chromic [second stage], boric, carbonic, and silicic), and have seen that basic precipitates generally begin to form as soon as the pH values required for the precipitation of their respective hydroxides have been attained.

As weak organic acids are often encountered in analytical work, and moreover, as weak hydroxy acids, such as tartaric and citric, are sometimes introduced for the purpose of preventing the precipitation of certain bases, the author (*J. Chem. Soc.*, 1926, 269) has studied the nature of the reactions which they involve when their sodium salts are allowed to react upon various salt solutions. The sodium salts chosen were the acetate, oxalate, and the tartrate, and many of the experiments took the form of hydrogen electrode titrations. Brief reference will be made to the general results obtained.

Sodium Acetate Titrations.

As acetic acid has a small dissociation constant, $1 \cdot 8 \times 10^{-5}$, it was thought that the hydrion concentrations produced during some reactions would be so low that the pH would be attained at which the hydroxides are precipitated, and it was expected, therefore, that basic acetates would be obtained from solutions of salts of the weakest bases. Salt solutions of zirconium, thorium, and chromium were studied.

In every case, the hydrogen-ion concentrations indicated when an excess of sodium acetate had been added were well buffered due to the equilibria established between the sodium acetate and the considerable proportions of acetic acid which had failed to combine. The normal hydroxide pH values were exceeded in the zirconium and thorium reactions and yet, at ordinary temperatures, did not result in precipitation. There was considerable buffer

action in the chromium titration which prevented the attainment of the precipitation pH.   Nevertheless, the solutions were proved to contain highly basic aggregates in spite of the fact that they remained perfectly clear and yielded to complete decomposition often only after prolonged boiling.   Thus, it was found that the pH produced when 4 mols. of sodium acetate had been added to 1 mol. of zirconium chloride was such as would indicate that the following reaction had taken place :

$$4NaAc + ZrCl_4 + 3 \cdot 64H_2O \rightarrow ZrCl_{0 \cdot 36}(OH)_{3 \cdot 64}$$
$$+ 3 \cdot 64HAc + 0 \cdot 36NaAc.$$
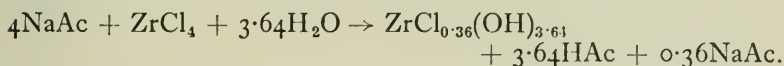
With further additions of sodium acetate the pH values obtained show that the basic chloride underwent complete decomposition to hydrated zirconia and liberated more acetic acid.   The solution was clear and its rate of decomposition on boiling appeared to be determined by the excess of sodium acetate.   There is every reason to believe that the action of sodium acetate on ferric chloride in analysis sets up similar pH changes, and though there is no pre- cipitation at ordinary temperatures the basic nature of the solution is evident from the characteristic red colour of the solution. With thorium chloride solution no precipitate was formed, but with a thorium sulphate solution a precipitate of basic sulphate appeared at the requisite pH, but it re-dissolved at a higher pH value when more sodium acetate had been added.   The basic acetate solutions of chromium are accompanied by remarkable changes in colour and, indeed, in their chemical properties.   It is probable that the true explanation is to be found in the colloidal nature of the solu- tions and not to the existence of salts of various " acetato-chrom- ium " bases suggested by Weinland and Büttner (*Z. anorg. Chem.*, 1912, **75,** 293), and which they consider to be in accordance with the " co-ordination theory."   It is interesting that the five so- called bases are basic acetates, and contain varying amounts of acetate, *viz.*, 2·67, 2·33, 2·17, 2, and 1·5 equivalents to each atom of chromium.

Sodium Oxalate Titrations.

Though oxalic acid is a fairly strong acid in regard to its first stage of ionisation, it is comparatively weak in respect to its second stage, K_2 being $1 \cdot 3 \times 10^{-4}$.   The influence which this has on the reactions between sodium oxalate and salts of weak bases will now be discussed.   It is significant that the hydroxides which are generally supposed to enter into complex formation with oxalates are those of weak bases, all of which are precipitated by alkalis

from solutions whose hydrion concentrations are greater than 10^{-7} (compare Schäfer and Abegg, Z. anorg. Chem., 1906, **14**, 293). The reactions between zirconium chloride, chrome alum and aluminium sulphate and sodium oxalate were such that many of the hydrions arising from the second stage of dissociation of oxalic acid failed to react with the respective bases, for the curves corresponding to the addition of excesses of the reagent showed that buffering took place as the result of equilibria between hydro-oxalate-, HC_2O_4', and the added oxalate-ions. The inability of the hydrions from the second stage to react with zirconium hydroxide led to its precipitation as a basic oxalate at pH 1·7, but on adding a small excess of sodium oxalate the precipitate dissolved ($pH = 2$). The resulting solution tended to resist precipitation with alkalis, a property which is more marked in the case of complex chromium oxalate solutions. Whilst chromium oxalate does not appear to have been obtained in the crystalline form, it is an easy matter to prepare crystalline double oxalates of the alkali metals and chromium. A typical one is Gregory's salt, $3K_2C_2O_4,Cr_2(C_2O_4)_3,6H_2O$; solutions of which are not readily precipitated on adding alkali. The cause of the existence of these salts probably lies in the fact that the main reaction of chromium hydroxide with oxalic acid involves the first stage of its ionisation in forming $Cr(HC_2O_4)_3$; the second stage being that of too weak an acid to enter into combination to any extent. On treatment with strong bases, such as potassium or sodium hydroxides, the second stage of ionisation is brought into action with the formation of $Cr(KC_2O_4)_3$. Similar remarks apply to aluminium.

The non-precipitability of chromium oxalate solutions may probably be found to be due to the formation of relatively stable basic chromium oxalate complexes through the weakness and colloidal nature of chromium hydroxide coupled with the weak acid function of hydro-oxalate ions. It is certain that the supposed existence of salts of a hypothetical tribasic chromioxalic acid, in which the chromium is in the anion, supplies no real explanation of their resistance to alkalis. This hypothesis was advanced by Rosenheim in 1896, and its validity was later tacitly assumed by Werner for Gregory's salt in the development of his extension of the co-ordination theory known as " mirror-image isomerism " or sterioisomerism of inorganic compounds. Measurement of the hydrogen-ion concentrations of these complex oxalate solutions shed new light on their formation and constitution, which appears to be at variance with the assumption of the tribasicity of the so-called hypothetical chromioxalic acid, and therefore invalidates Werner's hypothesis in regard to its appli-

cation to Gregory's salt. The fugitive optical activity observed by Werner, Jaeger, Rideal, and Thomas after resolution by means of strychnine probably provides no substantial evidence for Werner's theory. Its disappearance seems to be connected with the hydrolysis of the salt on dissolution, and in the opinion of the author the real cause of the optical activity must be sought by considering the physico-chemical nature of the bases and the acid concerned. (See p. 263, and *J. Chem. Soc.*, 1926, 280.) It may be that the chromium oxalate complex at first retained some little strychnine which subsequently separated as the insoluble iodide.

Sodium Tartrate Titrations.

Tartaric acid is comparatively weak in its first stage of ionisation, $K_1 = 1.27 \times 10^{-3}$, and much weaker in its second stage, $K_2 = 9.65 \times 10^{-5}$ at 18° C. Fig. 74 shows the variations in

C.c. N/10-Sodium tartrate.
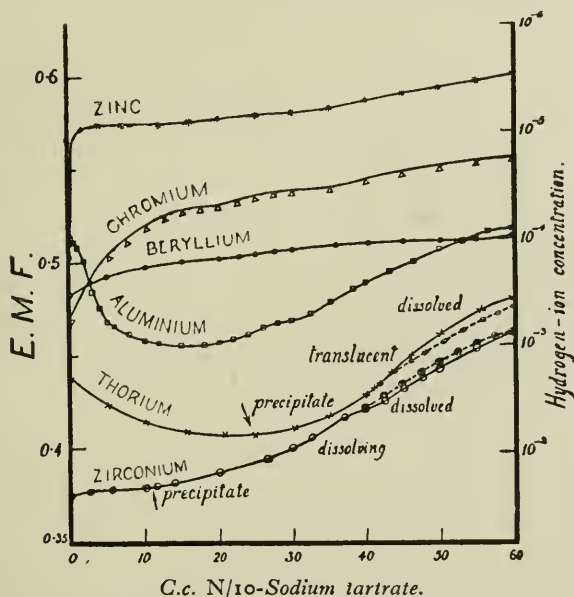
FIG. 74.—Interaction of Sodium Tartrate and Metallic Salt Solutions.

pH undergone when N/10-sodium tartrate is added to 100 c.c. of the following solutions : 0·01 M.-ZrCl$_4$, 0·01 M.-ThCl$_4$, 0·005 M.-Al$_2$(SO$_4$)$_3$, 0·025 M.-BeSO$_4$, 0·01 M.-Cr$_2$(SO$_4$)$_3$ as chrome alum, and 0·02 M.-ZnSO$_4$. In these titrations, basic tartrates were precipitated from the zirconium and the thorium chloride solutions only. They dissolved when an excess of the precipitant

had been added and yielded solutions from which the bases could not be precipitated with alkalis. The hydrogen-ion concentrations of these non-precipitable complex tartrate solutions seem to indicate that these basic precipitates on dissolving existed in the solutions as such. The existence of the other bases studied in these non-precipitable solutions seems to be likewise in the form of inert basic complexes. The fact that these basic complexes can exist in solution is most probably connected with the presence of hydroxy-groups in the acid. Thus the author has found that if dextrose be placed in a zirconium chloride solution on treatment with alkali the clear alkaline solution has an enhanced hydrogen-ion concentration through the presence of the zirconia. The reason for this increase is not clear, but it is likely that it must be due to some reaction having occurred between the zirconia and the hydroxyl-groups of the dextrose.

We shall now consider separately the curves shown in Fig. 74.

Zirconium.

A gelatinous basic tartrate began to be precipitated when 10 c.c. of sodium tartrate had been added (pH 1·66), but it began to redissolve on addition of 30 c.c. With 40 c.c. the solution was translucent, but became clear with 42·5 c.c.

In order to get some idea of the amount of titratable acid in these zirconium tartrate solutions, various quantities of $N/10$-sodium tartrate were added to 100 c.c. of $M/100$-zirconium chloride, and the resulting solutions titrated with $N/10$-sodium hydroxide. The results are in Table 85 : $a =$ c.c. of tartrate added, and b and $c =$ c.c. of $N/10$-alkali required to produce neutrality to phenol-phthalein at 18° and 100°, respectively.

TABLE 85.

a	.	.	10	20	30	40	60	80
b	.	.	33·2	33·1	33·0	33·1	33·2	33·2
c	.	.	34·9	34·6	35·0	34·3	34·1	34·2

The alkali produced a precipitate, which did not redissolve, from the solution to which 10 c.c. of sodium tartrate had been added, but the precipitates that formed initially in the 20 c.c. and 30 c.c. solutions redissolved when 25 c.c. and 14 c.c., respectively, of the alkali had been added. If no hydrolysis of the complex tartrate occurred, the table shows that, no matter how much sodium tartrate had been added, the quantity of free acid in the solution at 18° was equivalent to about 33·1 c.c. of $N/10$-sodium hydroxide, or 3·31 equivs. to 1 atom of zirconium. Under these

conditions, the simplest formula for the basic complex in these solutions is $ZrT_{0.35}(OH)_{3.3}$.*

To confirm the existence of this complex in solution, and to show that the free acid was tartaric, the following titration was made. The change in hydrion concentration which occurred after 40 c.c. of N/10-sodium tartrate had been added was what would be expected to occur on addition of sodium tartrate to a solution containing free tartaric acid only. A solution (140 c.c.) was therefore prepared containing 33.1 c.c. of N/10-tartaric acid, which appears to be the amount of acid liberated on addition of the first 40 c.c. of sodium tartrate in the zirconium titration. The E.M.F. of the solution, measured with the hydrogen electrode against the normal calomel electrode, was 0.422 volt (the E.M.F. for the corresponding stage of the zirconium titration was 0.421 volt). Increasing quantities of N/10-sodium tartrate were now added ; the voltages obtained are shown in the diagram by the broken line just above the zirconium curve. During the addition of the first 20 c.c. of N/10-sodium tartrate, *i.e.*, corresponding to 60 c.c. in the zirconium titration, the broken curve lay at a distance representing 3 milli-volts at most from the zirconium curve, but during the addition of the next 40 c.c. (*i.e.*, corresponding with 60 to 100 c.c. in the zirconium titration) the two curves became coincident.

Thorium.

The thorium curve in Fig. 74 is remarkable in that it shows that the addition of a normal tartrate rendered the solution more acid and then produced a precipitate. The pH of the original solution was 2.68, but had fallen to 2.15 on addition of 25 c.c. of sodium tartrate, when precipitation began. By analogy with the formation of other basic precipitates—chromates, borates, and carbonates—it would have been expected that the precipitation of a basic tartrate would not have taken place until the precipitation pH of the hydroxide had been attained, *viz.*, 3.5. A basic tartrate of thorium may also be precipitated by free tartaric acid ; precipitation began at pH 1.75 when 27.5 c.c. of 0.112 N-tartaric acid were added to 100 c.c. of M/100-thorium tartrate, the large hydrion concentration being no doubt due to hydrochloric acid produced by hydrolysis.

The precipitate obtained on addition of 30 c.c. of sodium tartrate was, when air-dried, amorphous and corresponded to the

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* T denotes $C_4H_4O_6$.

formula $ThO_2,0.69T,11.91H_2O$, or, the water content being disregarded, $ThT_{0.69}(OH)_{2.62}$.

Like basic zirconium tartrate, basic thorium tartrate redissolved when just above 40 c.c. of $N/10$-sodium tartrate had been added, *i.e.*, when the proportion was $2Na_2T : ThCl_4$. The acid liberated in the solution was equivalent to 26·2 c.c. of $N/10$-sodium hydroxide. Therefore, of the acid initially present as thorium chloride ($= 40$ c.c., expressed in terms of $N/10$-acid), 26·2 c.c. had been replaced by hydroxide and 13·8 c.c. by tartrate, and consequently the simplest formula of the basic thorium complex in the solution is

$$ThT_{0.69}(OH)_{2.62},$$
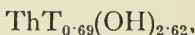
which happens to be also that of the precipitated basic tartrate. If it be assumed that 26·2 c.c. of $N/10$-tartaric acid were liberated during the interaction of 40 c.c. of $N/10$-sodium tartrate and 100 c.c. of $M/100$-thorium chloride, the concentration of the tartaric acid in the 140 c.c. of solution was 9.33×10^{-3}, and K_1 of tartaric acid being taken as 1×10^{-3} (the effect of K_2 is negligible —see page 150), the pH was 2·51. A solution (140 c.c.) of tartaric acid of this concentration was found, by means of the hydrogen electrode, to have exactly this pH. The solution was titrated electrometrically with $N/10$-sodium tartrate ; the titration curve, beginning at 40 c.c., is represented by the broken line lying a little below the thorium curve (Fig. 74). The differences in hydrogen-ion concentration shown in the two curves may have been due to some interaction between the basic tartrate and the tartaric acid while the former was dissolving.

These solutions do not yield precipitates when treated with alkalis. Non-precipitable solutions could also be prepared by using less sodium tartrate. From the solutions employed in the titrations alkalis produced complete precipitation if 1 mol. or less of either tartaric acid or sodium tartrate had been added for each mol. of thorium chloride. Although $1\frac{1}{2}$ mols. of sodium tartrate produced a precipitate, this dissolved on addition of alkali and the solution became non-precipitable. Basic thorium tartrate, as was the case with the zirconium precipitate, required a considerable excess of tartaric acid to redissolve it, and the basic complex in the acid solution appeared to be the same as that in the sodium tartrate solution.

The fact that basic thorium tartrate cannot be redissolved by alkali except in the presence of sodium tartrate suggests that sodium tartrate or partly neutralised tartaric acid is responsible for its dissolution. It can scarcely be attributed to the formation

of salts of a complex acid, and yet it seems to be due to some reaction taking place between the basic complex and the tartrate-ions when present in sufficiently large concentrations. A tartaric acid solution, on being gradually neutralised with alkali, therefore acquires a correspondingly increasing solvent capacity for both basic zirconium and basic thorium tartrates.

Aluminium.

Fig. 74 shows that in the aluminium titrations an unexpected increase in hydrion concentration occurred during the addition of the first 30 c.c. of tartrate solution ($= 3$ mols.). No precipitate separated and the solution remained clear. Hence, as the sodium tartrate was added, and sodium sulphate thereby formed, a considerable quantity of tartrate-ions, instead of combining with the aluminium, was set free to form hydrotartrate-ions, some free acid, and a basic aluminium tartrate complex in the solution. The maximum hydrion concentration, $10^{-3.02}$, was attained when 15 c.c. of sodium tartrate solution had been added. This concentration was probably due mainly to hydrogen-ions from the first stage of dissociation of the tartaric acid, the hydrotartrate-ions having reacted with the aluminium hydroxide.

Titrations were made of the acid liberated in the solutions obtained by adding various quantities of N/10-sodium tartrate to 100 c.c. of M/200-aluminium sulphate. Ten c.c. of sodium tartrate were insufficient to produce a solution non-precipitable by alkali, but when 20 c.c. [$i.e.$, 2 mols. Na_2T for 1 mol. $Al_2(SO_4)_3$] or more were used, the solutions became non-precipitable and the amounts of alkali required to give neutrality to phenol-phthalein varied from 2·4 to 2·7 equivalents (for 1 Al). In the boiling solutions, 2·8 equivalents produced neutrality in each case. Therefore, both in cold and in hot solutions a little tartrate remained firmly bound to the aluminium hydroxide. These experiments again seem to show that the non-precipitability is due to the existence of stable basic tartrates, the compositions of which, in the solutions studied, varied from $AlT_{0.3}(OH)_{2.4}$ to $AlT_{0.1}(OH)_{2.8}$.

Beryllium.

A small diminution in the hydrogen-ion concentration occurred in the titration of beryllium sulphate with sodium tartrate. This was not due to the formation of a less hydrolysed beryllium tartrate, for, as is shown by the curve (Fig. 74), no distinct change in hydrogen-ion concentration occurred when the requisite amount of sodium tartrate (50 c.c.) had been added. The small variation

in the hydrion concentration was caused by equilibria set up between the added tartrate-ions and the hydrotartrate-ions, which, by failing to react with the beryllium, left it in the solution in the form of a basic tartrate. The large concentration of hydrotartrate-ions was evidently due to their incapacity to react with that part of the beryllium hydroxide which gives rise to " soluble basic salts."

Solutions which contained one or more mols. of beryllium sulphate to one of sodium tartrate were completely precipitated by alkali, although solutions containing the reactants in the molar ratio 1 : 2 did not yield precipitates. The amounts of titratable acid in the complex tartrate solutions were approximately 1·53 equivalents for each molecule of beryllium sulphate taken, and consequently the composition of the final basic complex may be expressed by the formula $BeT_{0·24}(OH)_{1·53}$.

Chromium.

The hydrogen-ion concentrations shown in the chrome alum curve indicate that the amount of hydrotartrate ions liberated was less than that in the case of the corresponding beryllium titration. The difference appears to be accounted for by the fact that, although the precipitation pH, 5·69, of beryllium hydroxide is a little higher than that of chromium hydroxide, 5·34, one-half of the beryllium hydroxide molecule is associated with the formation of soluble basic salts as compared with one-third in the case of chromium, and consequently a larger equivalent amount of acid is rendered available for reaction. The sodium tartrate caused the violet chromium salt solution to turn green.

The formation of complex chromium tartrate solutions which are not precipitable by alkali depends not so much on the amount of sodium tartrate added as on the treatment to which the solutions have been subjected, and in this respect they appear to be similar to that of complex oxalate solutions. There is, however, the one difference that whereas oxalate solutions, on prolonged boiling with alkali, yield a precipitate, those of chromium tartrate in general do not. Chromium tartrate solutions, on boiling, become purplish-red, but if they are then treated with alkali at room temperature they turn green as soon as the precipitation pH of the hydroxide is reached. As in the case of oxalate solutions, boiling caused the liberation of acid and the simultaneous formation of inert basic salt.

Zinc.

Although in the zinc sulphate titration the sodium tartrate did not precipitate zinc hydroxide, the hydrion concentration on

addition of the first 40 c.c. (when the molecular ratio was Na_2T : $ZnSO_4$) was reduced to nearly the precipitation pH, 5·2, of zinc hydroxide. Titrations were made with sodium hydroxide and phenol-phthalein of the acid liberated when varying quantities of N/10-sodium tartrate were added to 100 c.c. of M/50-zinc sulphate ; the results are in Table 85A, where a = mols. of sodium tartrate per mol. of zinc sulphate, and b and c = equivs. of sodium hydroxide required to produce precipitate and neutrality, respectively.

TABLE 85A.

a		2	2·5	3	4	5
b		0·41	1·00	—	—	—
c		1·14	1·13	1·19	1·14	1·03

The table shows that the minimum quantity of sodium tartrate required to prevent precipitation by alkali was 3 mols. for 1 mol. of zinc sulphate (= 120 c.c.). This quantity is much greater than those required in the case of the weaker bases. Moreover, all the solutions referred to in the table gave a precipitate when boiled with alkali. The change in hydrion concentration after 40 c.c. of sodium tartrate solution had been added shows that not all the hydrions of the tartaric acid had reacted, and the amounts of alkali required to neutralise the acid which had failed to react indicate that the compositions of the basic tartrates in the complex solutions varied from $ZnT_{0·49}(OH)_{1·03}$ to $ZnT_{0·41}(OH)_{1·19}$.

Lanthanum.

The complex lanthanum tartrate solutions which are non-precipitable with alkali constitute an excellent example of the solutions being composed of basic tartrate complexes.

Lanthanum tartrate, $La_2(C_4H_4O_6)_3,12H_2O$, although insoluble in water, is so readily soluble in mineral acids that when tartaric acid is added to a solution of a lanthanum salt of a strong acid no precipitate is formed ; but one is obtained from a solution of lanthanum acetate. It is also readily soluble in alkalis and dissolves in an excess of sodium tartrate or tartaric acid solution. The author has found that the non-precipitable solutions formed by the solution of lanthanum tartrate in alkali contain basic tartrate ranging in composition from $LaT_{0·90}(OH)_{1·20}$ to $LaT_{0·59}(OH)_{1·82}$.

The foregoing observations show that complex tartrate solutions are essentially basic in nature. This is especially evident in the cases of the complex zirconium and thorium tartrate solutions

produced by the re-solution, probably without change in com-
position, of the basic tartrates first precipitated. Unlike the com-
plex solutions which were sometimes formed with acetates and
oxalates, those of the tartrates are extremely stable. The basic
tartrates, like the basic aggregates in solution, are strongly resis-
tant to alkalis, which probably explains their non-precipitability
by such means.

The existence of these basic tartrate complexes would also
account for the properties of Fehling's solution. The fact that
the ease of reduction to cuprous oxide is comparable with that of
freshly precipitated cupric hydroxide suggests that the condition
of the cupric salt in alkaline tartrate solutions is in some way
related to that of cupric hydroxide itself, as would obtain in basic
tartrate complexes.

The condition of copper tartrate on passing into these complex
alkaline tartrate solutions is, at any rate, basic. For example,
Kahlenberg (*Z. physikal. Chem.*, 1895, **17**, 586), Masson and Steele
(*J. Chem. Soc.*, 1899, **75**, 725), and Pickering (*ibid.*, 1911, **99**, 169)
found that the quantity of sodium or potassium hydroxide necessary
to produce alkalinity in a solution of copper tartrate varied from
$1 \cdot 25$ to $1 \cdot 36$ mols., and therefore the basic complexes in the solu-
tions must have varied from $CuT_{0 \cdot 38}(OH)_{1 \cdot 25}$ to $CuT_{0 \cdot 32}(OH)_{1 \cdot 36}$.

Previous workers attempted to account for the anomalies of
complex tartrate solutions by regarding the heavy metal as being
present in a complex anion. Masson and Steele obtained a
substance, $K_3Cu_4C_{12}H_7O_{18},5H_2O$, by precipitation with alcohol
from a copper tartrate solution which had been neutralised with
$1 \cdot 25$ equivalents of potassium hydroxide. The substance, which
was isolated as a dark blue, gummy mass (and therefore was of
questionable character), was in effect composed of $3K_2T$ and
$8CuT_{0 \cdot 375}(OH)_{1 \cdot 25}$ and was probably a mixture of potassium tar-
trate with a preponderance of basic copper tartrate. Their mi-
gration experiments on solutions of this substance are important
in that they show that some copper had passed into the portion
carrying the negative charge, but this may have been due equally
well to the colloidal nature of the basic copper tartrate as to the
presence of a complex copper anion. Pickering also obtained
flocculent precipitates from copper tartrate solutions by adding
alcohol. The unwashed precipitates (whose constitutions he tried
to establish by regarding some of the copper as quadrivalent)
contained variable quantities of potassium salt, all of which, to-
gether with some copper, could be removed by washing.

CHAPTER XVIII.

PRECIPITATION OF NORMAL AND BASIC PHOSPHATES.

The Precipitation of Phosphates.

As found on page 146 phosphoric acid behaves in its first stage of ionisation as a strong acid, $K_1 = 9{\cdot}4 \times 10^{-3}$, in its second as a weak acid, $K_2 = 1{\cdot}4 \times 10^{-7}$, and in its third stage as an extremely weak acid, $K_3 = 2{\cdot}7 \times 10^{-12}$, so weak that its dissociation can only just be determined. It appears probable, from the very low order of magnitude of K_3, that the third hydrogen atom of phosphoric acid might be incapable of reacting with the majority of weak bases unless the phosphates happen to be very insoluble and the phosphate-ion concentrations of the mother-liquors are kept sufficiently large to exceed the solubility products without permitting the hydrogen-ion concentrations to become so small as to cause precipitation of the hydroxides. The author (*J. Chem. Soc.*, 1927, 614) studied the influence of K_3 in various precipitation reactions by means of the hydrogen and normal calomel electrodes in the usual manner. Two series of potentiometric titrations were made : the first comprising the reactions between solutions of phosphoric acid and strong bases, *viz.*, the hydroxides of sodium, calcium, barium, and strontium ; and the second series dealing with the action of trisodium phosphate, chosen because it involves the third stage of ionisation, on solutions of salts of typical metallic bases. A titration by lime water of phosphoric acid in a solution of sucrose was included in the first series in view of the discordant observations of Wendt and Clarke (*J. Amer. Chem. Soc.*, 1923, **45,** 881) and Hoffman and Gortner (*J. Physical Chem.*, 1925, **29,** 769). [See also Holt, LaMer, and Chown (*J. Biol. Chem.*, 1925, **64,** 509) and Farnell (*J. Soc. Chem. Ind.*, 1926, **45,** 343T)], and also on account of its importance in sugar refining (p. 397).

I. Phosphoric Acid and Alkaline Earths.

In Fig. 41 on page 146 the titration curves at 20° C. of phosphoric acid with the alkaline earths are compared with one obtained by using sodium hydroxide. The solutions used were (1) 100 c.c.

of 0·00965 M.-H_3PO_4 with 0·0558 N-Ba(OH)$_2$, (2) 100 c.c. of 0·00765 M.-H_3PO_4 with 0·0359 N-Sr(OH)$_2$, (3) 100 c.c. of 0·01024 M.-H_3PO_4 with 0·0447 N-Ca(OH)$_2$, and (4) 100 c.c. of 0·01024 M.-H_3PO_4 containing 5 g. of sucrose with 0·0447 N-Ca(OH)$_2$. With the exception of the sodium hydroxide titration and the alkaline earth titrations up to the addition of the first equivalent, the E.M.F's recorded were not true equilibrium values, but were those indicated immediately after each addition of the reactant, for, as Wendt and Clarke observed in their lime-water titrations, the initial P.D's become smaller when the solutions stand for some time, through the slow reactions which take place between the precipitate and the added alkaline earth.

On comparing the alkaline-earth titration curves, up to the points corresponding to the beginning of precipitation, with that of sodium hydroxide, it will be seen that they cover almost identical ranges of hydrogen-ion concentration. In the lime-water titration precipitation was delayed until 1·53 equivs. (= 35 c.c.) had been added and pH 6·72 was attained. On standing over-night, a solution of the same concentrations deposited an appreciable amount of precipitate and its pH fell to 5·98 ; in fact, precipitates were formed when solutions were allowed to stand which contained only just over 1 equiv. of calcium hydroxide. The delay in precipitation and the high initial pH were caused by neutralisation taking place immediately, whereas the precipitation from the supersaturated solution was a matter of time. Had neutralisation only taken place, the hydrogen-ion concentration would have been equal to $[H_2PO_4'] \times K_2/[HPO_4''] = (2 - n) \times 1·4 \times 10^{-7}/(n - 1)$, where n is the number of equivs. of alkaline earth, from which it follows that the pH of the calcium solution when on the point of precipitation should have been 6·91, which is slightly higher than the observed value, 6·72, the difference evidently being due to the precipitation reaction having proceeded to a small extent. The presence of sucrose in the phosphoric acid solution did not impede precipitation. In the baryta titration, 1·62 equivs. were required to start precipitation, which took place at pH 6·88 ; on standing over-night further precipitation occurred and the pH of the solution fell to 6·07. Strontium hydroxide solution produced a precipitate with 1·78 equivs. (38 c.c.) ; the pH was then 7·34, but it became 6·60 after standing over-night, more precipitate having separated. These titrations up to the point of precipitation consisted chiefly of neutralisation, for by calculation it is found that for neutralisation alone the pH should have been 7·07 in the barium titration instead of 6·88 observed, and 7·40 in the strontium titration instead of 7·34.

The precipitates first formed were the monohydrogen phosphates, $M^{\cdot\cdot}HPO_4$, which by the addition of more alkaline earth became converted into the normal phosphate, $M_3(PO_4)_2$. The inflexion in the baryta-titration curve occurred during the addition of the third equiv., and therefore the precipitate was a mixture of di- and tribarium phosphates, whereas in the strontia curve the inflexion was not produced until the third equiv. had been added, showing that the precipitate was the normal strontium phosphate. The final inflexion in the calcium hydroxide titration occurred when the third equiv. had been added, suggesting that at that stage the precipitate was tricalcium phosphate. It will, however, be observed that further additions of lime water did not cause as great an increase in pH as in the other titrations. This was due to the absorption by the calcium phosphate of some calcium hydroxide thus rendering the phosphate basic. Bassett (*J. Chem. Soc.*, 1917, **111,** 620) found that one molecule of tricalcium phosphate can absorb one-third of a molecule of calcium hydroxide to form " hydroxyapatite," $3Ca_3(PO_4)_2,Ca(OH)_2$; he believes that this is the calcium phosphate which can permanently exist in the soil under ordinary conditions.

The variation in hydrogen-ion concentration, which occurred in the lime-water reaction just after two equivs. had been added, is remarkable in that the addition of more reactant actually caused an increase in the concentration of hydrogen-ions. It appears probable, therefore, that the added calcium hydroxide reacted with the dicalcium phosphate remaining in solution causing precipitation of the tricalcium salt, and in so doing it also decomposed the supersaturated solution, precipitating some dicalcium salt and possibly a little of the normal salt in accordance with the equation suggested by Wendt and Clarke : $4CaHPO_4 = Ca_3(PO_4)_2 + Ca(H_2PO_4)_2$. The pH data calculated from the phase-rule data of Bassett (*vide infra*) show that both the di- and the tri-calcium phosphates attain equilibrium with liquid phases whose pH's are about 5·5 through equilibria involving H_2PO_4' and HPO_4'' ions, the former being in considerable excess. It would be expected, therefore, that a pH of 5·5 would represent the lowest value to which this downward inflexion could attain, and it is interesting to find that this is about the value shown by Wendt and Clarke's curve. The higher pH obtained by the author was due to insufficient time being allowed for the attainment of final equilibrium. The earlier appearance of the inflexion in Wendt and Clarke's curve was due to the precipitation of the two phosphates of calcium. They found, by allowing 10 days for the attainment of equilibrium, that the curve became rectilinear during the addition of the greater part of the second and

third equivs. of calcium hydroxide, and indicated hydrogen-ion concentrations varying from pH 5·5, when a little more than the first equiv. had been added, to pH 6·0 at 2·5 equivs. This is as would be expected from a consideration of Bassett's work (*vide infra*). Farnell obtained similar results by boiling the solutions and cooling to 20° before measuring the pH. By allowing the solutions to stand over-night in stoppered bottles, the author found that the change in hydrogen-ion concentration was gradual and varied from pH 5·98 at 1·53 equivs. to pH 6·52 at 2·5 equivs. These precipitations had not, however, become complete.

The titration curve of phosphoric acid in presence of sucrose given in Fig. 41 shows that sucrose acts as a buffer in preventing an increase in hydrogen-ion concentration.

The considerable amount of supersaturation, with its consequent effect on the hydrogen-ion concentration, which occurs when alkaline earths are added to phosphoric acid solutions, renders it difficult to ascertain, by means of a titration method, when a precipitate begins to separate. The pH at which calcium begins to separate as a phosphate is of some importance in the chemistry of soils, and therefore certain data relating to the ternary system $CaO–P_2O_5–H_2O$ obtained by Bassett (*J. Chem. Soc.*, 1917, **111**, 624; *Z. anorg. Chem.*, 1908, **59**, 1) at 25° and by Cameron and Bell (*J. Amer. Chem. Soc.*, 1905, **27**, 1512) have been studied with respect to the stage of neutralisation of the phosphoric acid in the liquid phases; then, either by comparison with the neutralisation curve (Fig. 41), or by calculation, an approximate estimate has been made of the hydrogen-ion concentrations of the liquid phases in equilibrium with solid phases containing varying amounts of phosphate. Table 86 was compiled from Bassett's data.

It will be seen from the table that those liquid phases which contained 0·149 per cent. P_2O_5 (= 0·02 M.-H_3PO_4) or less, as a rule contained calcium hydroxide sufficient to neutralise about 5 per cent. of the second stage, giving hydrogen-ion concentrations of the order of $10^{-5.5}$. The amount of lime became in excess of 2 equivs. for liquid phases containing less than 0·00613 per cent. P_2O_5 (= 0·0009 M.-H_3PO_4). The solid phases which were more basic than $CaHPO_4$ are indicated by the molar ratio PO_4/CaO, which is 0·67 for tricalcium phosphate and 0·60 for the substance, hydroxyapatite, $3Ca_3(PO_4)_2,Ca(OH)_2$. The values of the ratio suggest that the solid phases in equilibrium with the most dilute liquid phases were hydroxyapatite, whereas the ratios corresponding to the more concentrated liquid phases fall, with one exception, between 0·66 and 0·95, proving that the solid phases were either mixtures of tri- and di-calcium phosphate, or possibly

TABLE 86.

ANALYSIS OF BASSETT'S DATA OF THE SYSTEM CaO–P_2O_5–H_2O.

Per Cent. CaO.	Per Cent. P_2O_5.	Solid Phase.	Per Cent. Neutralised.*		pH.
1·181	3·613	$CaHPO_4$	83	(I)	3 approx.
0·826	2·387	,,	81	(I)	3 ,,
0·165	0·417	{ $CaHPO_4$ and $CaHPO_4, 2H_2O$ }	0·04	(II)	—
0·0696	0·178	$CaHPO_4, 2H_2O$	99·6	(I)	—
0·0617	0·149	,,	5·1	(II)	5·6
0·0507	0·121	,,	6·3	(II)	5·7
0·0485	0·119	,,	3·3	(II)	5·4
0·0427	0·105	,,	3·1	(II)	5·4
		PO_4/CaO in solid phase.			
0·0406	0·0980	0·76	5·1	(II)	5·6
0·0389	0·0947	0·79	4·1	(II)	5·5
0·0373	0·0897	0·95	5·5	(II)	5·6
0·0326	0·0777	0·62	6·4	(II)	5·7
0·0299	0·0727	0·67	4·4	(II)	5·5
0·0269	0·0607	0·66	12·4	(II)	6·0
0·0191	0·0465	0·70	4·1	(II)	5·5
0·0175	0·0423	0·71	4·9	(II)	5·6
0·0174	0·0414	0·69	6·5	(II)	5·7
0·0167	0·0405	0·69	4·6	(II)	5·5
0·0126	0·0332	—	96	(I)	—
0·0122	0·0302	0·66	2·4	(II)	5·2
0·00893	0·0196	0·63	12·0	(II)	6·0
0·00582	0·0134	0·62	10·1	(II)	5·9
0·00600	0·00613	0·62	4·9	(III)	11 approx.

di-calcium phosphate in various stages of decomposition. The presence of two solid phases *in equilibrium* with variable liquid phases is incompatible with the phase rule, and it is considered that the conversion of di-calcium phosphate into the normal salt is very slow owing to the ionic requirements of the one being set up simultaneously with those of the other. Consequently, the solid phases may have been indefinite and unstable mixtures, although it appeared, as far as could be ascertained experimentally, that equilibrium had been established.

Action of Trisodium Phosphate on Metal Salt Solutions.

The variation in hydrogen-ion concentration which occurred at 20° when a N/10-solution of trisodium phosphate was added to 100 c.c. of the salt solutions (Table 87) was followed electro-metrically. The E.M.F's were reproducible, except in the final

* The Roman numerals (I), (II), and (III) relate to the first, second, and third stages, respectively.

stages of the chromium and magnesium titrations. Table 87 also contains the pH's at which the phosphate precipitates began

TABLE 87.

Solution Titrated.						Phosphate pH.	Hydroxide pH.
0·02 M.-MgSO$_4$	.	.	.	.	.	9·76	10·49
0·0358 M.-CaCl$_2$	.	.	.	.	.	7·00	—
0·02 M.-MnCl$_2$.	.	.	.	.	.	5·76	8·43
0·02 M.-ZnSO$_4$.	.	.	.	.	.	5·66	5·20
0·00667 M.-Cr$_2$(SO$_4$)$_3$, K$_2$SO$_4$		.	.	.		$\begin{cases} 4\cdot62 \\ 5\cdot65 \end{cases}$	5·34
0·00667 M.-Al$_2$(SO$_4$)$_3$.	.	.	.	.	.	3·79	4·14
0·02 M.-BeSO$_4$.	.	.	.	.	.	3·41	5·69
0·01 M.-ThCl$_4$.	.	.	.	.	.	2·72	3·51
0·01 M.-ZrCl$_4$.	.	.	.	.	.	1·57	1·86

to separate, and, for purposes of comparison, the respective hydroxide pH's.
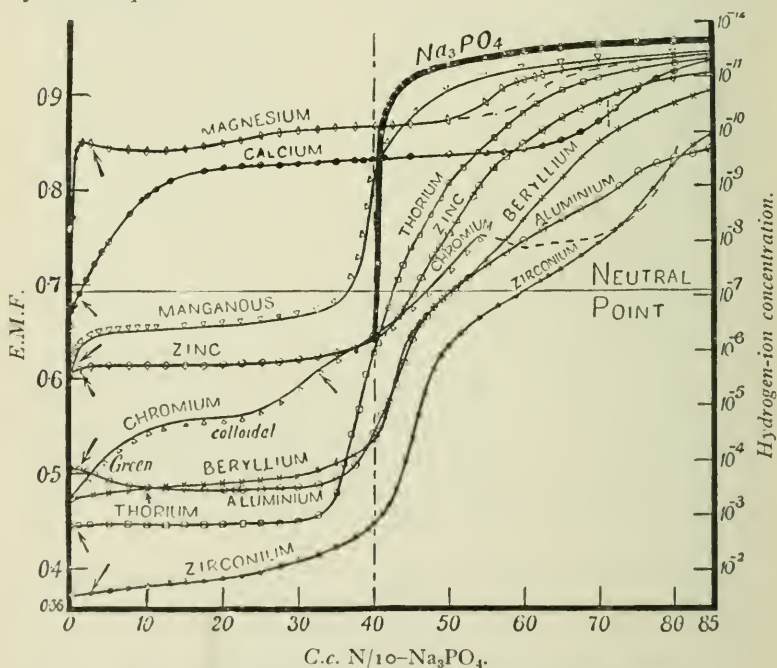
FIG. 75.—Precipitation of Normal and Basic Phosphates.

The curves showing the hydrogen-ion concentrations acquired when increasing amounts of trisodium phosphate had been added are given in Fig. 75. The amount of trisodium phosphate

required to form the normal metallic phosphate was 40 c.c. in every case except that of calcium chloride, in which it was 71·6 c.c. The curve marked Na_3PO_4 was obtained by adding N/10-sodium phosphate solution to 140 c.c. of solution (i.e., the volume attained in the precipitation reactions when stoichiometrical amounts of the phosphate solution had been added) containing an amount of sodium chloride equal to the amount of neutral salt formed in the precipitation reactions with 40 c.c. of sodium phosphate. It would therefore represent the variation in hydrogen-ion concentration on adding an excess of the reactant, if the pure normal phosphates had been precipitated, leaving in solution amounts of phosphate so small as to exert no " buffer action." The arrows denote the beginning of precipitation.

In no instance did the curve corresponding to an excess of the reactant coincide with this curve, the two nearest being those of manganese and calcium. The others are widely divergent. The pH data given in Table 87 show that the phosphate precipitates, with the exception of that of zinc, separated from solutions whose hydrogen-ion concentrations were greater than those requisite for the precipitation of the corresponding hydroxides ; and thus it appears that, whilst it may be possible to obtain the normal phosphates by the use of an amount of trisodium phosphate insufficient to give complete precipitation, yet as soon as sufficient reactant has been added to bring the pH of the solution to that necessary for the precipitation of the hydroxide, any metallic salt remaining in solution will then be precipitated, and, moreover, there will be a strong tendency for the precipitate to be decomposed. That some such reaction must have taken place is evident from the curves. The depression of the manganese and the calcium curves must have been caused by the " buffer action " of the added sodium phosphate on the HPO_4'' ions, which had been supplied to the solutions by the precipitates. The greater hydrogen-ion concentrations set up in the zinc, beryllium, aluminium, and thorium reactions were, as may be seen from the sodium hydroxide curve in Fig. 75, of the same magnitude as those produced in the second, and subsequently the third, stage of neutralisation. Hence the precipitates must have decomposed to furnish the mother-liquor with H_2PO_4' ions, some of which, by reacting with the added phosphate, became converted into HPO_4'' ions.

No inflexion occurred in the zirconium chloride reaction when the stoichiometrical quantity of sodium phosphate had been added, though one appeared on the addition of a small excess. By comparing the range of hydrogen-ion concentrations produced during the addition of this excess with that obtained towards the end of

the neutralisation of the first stage of phosphoric acid (Fig. 41), it will be seen that the equilibria which produce these relatively large concentrations of hydrogen ions involve some free phosphoric acid. This must have been liberated through the extreme weakness of zirconium hydroxide, with the result that a highly basic zirconium phosphate was precipitated, the formation of which might have been expected from the fact that zirconium chloride solutions are very considerably hydrolysed. Thus it was found (Britton, *J. Chem. Soc.*, 1925, **127**, 2133) that a freshly prepared solution of the concentration used in this titration was hydrolysed to the extent of 54 per cent., and consequently the free acid liberated an equivalent amount of phosphoric acid on reacting with trisodium phosphate. The middle point of the first inflexion (corresponding with the addition of 45 c.c., an excess of 5 c.c.) represents the stage when the liberated phosphoric acid had reacted with the added phosphate to form monosodium phosphate, in accordance with the equation $Na_3PO_4 + 2H_3PO_4 = 3NaH_2PO_4$, from which it follows that the excess of 5 c.c. reacted with twice the amount, *i.e.*, 10 c.c. of phosphoric acid. The total amount of phosphoric acid was equivalent to 40 c.c., and of this 13·3 c.c. corresponded to the first stage of dissociation. The amount of phosphoric acid which had escaped precipitation was therefore 10/13·3 of the quantity required for the normal phosphate of zirconium, and hence the composition of the precipitate might be represented as $6ZrO_2, P_2O_5$. The curve obtained on adding a further excess of the reactant, instead of being sharply inflected through pH 9 owing to the complete formation of disodium phosphate, showed that a considerable " buffer action " occurred between pH 6 and 10. It appears, therefore, from the expression $[H^.] = K_2 . [H_2PO_4']/[HPO_4'']$ governing the hydrion concentrations during the second stage of neutralisation, that the precipitate itself, in being decomposed, must have exerted some buffering action by imparting to the mother-liquor a small but continuous concentration of H_2PO_4' ions.

The precipitation curve of aluminium phosphate is interesting in that the first addition of sodium phosphate caused an increase in the concentration of hydrogen-ions, reaching a maximum at pH 3·43 with 17·5 to 20 c.c. The precipitate became very basic when an excess of sodium phosphate was added as shown by the comparatively large buffering effect—at 80 c.c. the pH was 9·41 ; at 100 c.c., 10·02 ; at 120 c.c., 10·24 ; and at 140 c.c., 10·33. The hydrolysis of the precipitate into aluminium hydroxide was accompanied by its gradual dissolution in the sodium phosphate solution. Thus the solution became translucent with 80 c.c. and quite clear with 140 c.c. Reference to the hydrogen-ion concentration curve

showing the action of alkali on aluminium sulphate solution (p. 258) indicates that sodium aluminate began to form when the pH became between 9 and 10. Hence it appears that the dissolution of the precipitate in an excess of sodium phosphate was due to the formation of sodium aluminate, the necessary free alkali being furnished by the trisodium phosphate through the exceptional weakness of phosphoric acid in its third stage of ionisation and the resulting hydrolysis of its sodium salt. The inability of disodium phosphate, when added in excess, to cause the precipitate to dissolve is due to the low pH which it sets up. An excess of this precipitant reduces the hydrogen-ion concentration considerably below that at which aluminium hydroxide becomes precipitable, causing the precipitate to hydrolyse. Thus Munroe (*Amer. J. Sci.*, 1871, (iii), **1**, 329) found that a precipitate, $AlPO_4,Al(OH)_3$, $2 \cdot 5H_2O$, was obtained when an alum solution was treated with an excess of the disodium salt.

Although precipitation did not take place from the beryllium sulphate solution until 7·5 c.c. of sodium phosphate had been added, the delay was not accompanied by any great change in hydrogen-ion concentration. As mentioned above, the final beryllium precipitate was a basic phosphate. Bleyer and Müller (*Z. anorg. Chem.*, 1913, **79,** 263) assigned the formula BeO, $2Be_3(PO_4)_2,13H_2O$ to a precipitate similarly obtained. The effect of the soluble basic salt formation was not apparent in the beryllium sulphate reaction, which was very probably connected with the slight solubility of beryllium phosphate originally precipitated. The influence, however, was marked in the chromium titration. At first the sodium phosphate merely caused the violet solution to turn green—a point of importance in connexion with the question of the colours of chromium salt solutions, and one which is always observed whenever a violet chromium salt solution is rendered basic. Simultaneously an appreciable decrease in hydrogen-ion concentration occurred until 12 c.c. ($=$ 0·90 equiv. per atom of Cr) had been added, pH $=$ 4·62, a cloudiness then being observed. For the next 10 c.c. the pH remained nearly constant, although the solution became more and more colloidal, and thereafter a steady rise in pH occurred, coagulation taking place at pH 5·65 with 32·5 c.c. ($=$ 2·44 equivs.). The bulk of the precipitate was green and flocculent, but it contained a small quantity of a violet crystalline precipitate, apparently the normal chromium phosphate. The delay in precipitation is significant, as also is the fact that when it took place the hydrogen-ion concentration of the mother-liquor was not very far from that at which chromium hydroxide is precipitated, *viz.*, pH 5·3. The diminu-

tion in hydrogen-ion concentration was gradual until 54 c.c. (= 4·05 equivs.) of sodium phosphate had been added, $pH = 8·07$, at which stage the E.M.F's not only became very unsteady, but also showed a remarkable increase in hydrogen-ion concentration. The changes which took place immediately after the addition of each new amount of sodium phosphate are shown by the broken line. The hydrogen-ion concentration subsequently grew smaller, such that when 80 c.c. had been added the pH had become 9·71. Precipitation became complete just after the stoichiometrical amount of sodium phosphate, 40 c.c., had been added. The change in pH with the excess of reactant shows that a basic phosphate had been precipitated, and the exceptional change after 4 equivs. of sodium phosphate had been added indicates that the precipitate underwent rapid hydrolysis.

The pH, 5·66, at which the zinc phosphate precipitate began to form was a little higher than that required by zinc hydroxide, *i.e.*, 5·20, but reference to the hydroxide precipitation curve shows that the pH during the main part of the precipitation was 6, whereas the phosphate curve shows a slightly lower pH, *viz.*, 5·7.

The E.M.F's recorded in the reaction with calcium chloride up to the addition of 7 c.c. of sodium phosphate tended to be low initially but slowly increased to steady values ; for larger volumes of sodium phosphate the voltages given primarily appeared to be reproducible. The stoichiometrical amount of sodium phosphate was 71·6 c.c., and this, as seen from the curve, gave rise to a hydrogen-ion concentration which was represented by the point of inflexion corresponding to the completion of precipitation as the normal calcium phosphate. The greater part of the precipitation occurred between pH 9·5 and 10, and, as will be seen from the sodium hydroxide titration curve (Fig. 41), such a pH corresponds to equilibria involving a predominance of HPO_4'' and very few PO_4''' ions, thus $HPO_4'' + OH' \rightleftharpoons PO_4''' + H_2O$, which must have been given by the hydrolysis of the tricalcium phosphate. The difference between the pH's which prevailed in this reaction and that during the precipitation from phosphoric acid (p. 326) is due to the suppression of the hydrolysis in the latter case by the small amount of partly neutralised phosphoric acid present, whereas this was absent in the double decomposition.

The precipitation from the magnesium sulphate solution is of interest for two reasons. Firstly, the inflexion indicating the end of precipitation did not appear when the stoichiometrical amount of sodium phosphate had been added, *viz.*, 40 c.c., but occurred with about 1½ times that quantity. Secondly, the solution from which the precipitate had separated was even more alkaline than

that in the calcium reaction, the pH at which the precipitate began to form being 9·76. The exact incidence of the inflected part depended on the efficiency of agitation of the reaction mixture and on the time allowed before measuring the E.M.F. The broken line was obtained by allowing longer time, and the inflexion began at 60 c.c., whereas the first curve was undergoing inflexion with that amount. A pH of 9·76 must have been produced by the same kind of ionic equilibria as in the calcium phosphate precipitation, in which, however, there was a greater proportion of phosphate ions. The amount of sodium phosphate required to effect precipitation suggests the reaction $MgSO_4 + Na_3PO_4 + H_2O = MgHPO_4 + NaOH + Na_2SO_4$, but the fact that the pH remained almost stationary at 10 throughout the course of precipitation shows that the concentration of free alkali was relatively small. The precipitate was $NaMgPO_4$, and it was therefore by its hydrolysis that the pH throughout its precipitation was determined.

Note on the Phosphate Separation.

The observations made in the course of these electrometric titrations afford a satisfactory explanation of the procedure adopted in qualitative analysis for the removal of phosphates. The phosphate precipitation pH's are functions of the concentrations of both the metallic and the phosphate ions, and the use of dilute solutions tends to keep the concentrations of both the bases and phosphoric acid comparatively small, and thereby fixes within narrow limits the pH at which the various phosphates are precipitated as the free acid is gradually neutralised and the solution made alkaline. The hydrogen-ion concentrations which prevailed during the formation of the phosphate precipitates (Fig. 75) are approximately those which would be set up if the phosphoric acid had been present in the solution and was subsequently neutralised with alkali. In the " basic acetate " method of removing phosphates, the solution, before treatment with ferric chloride solution, is buffered at about pH 5 by the acetic acid and an excess of either sodium or ammonium acetate. Fig. 75 shows that the only phosphates to be precipitated from solutions more acid than pH 5 are those of zirconium, thorium, aluminium, beryllium, and chromium. Ferric phosphate is also precipitated from very acid solutions. The phosphates and hydroxides which are precipitated from solutions of pH higher than 5 are those of zinc, manganese, calcium, and magnesium, to which should be added cobalt, nickel, strontium, barium, and many of the rare earths. It appears, therefore, that as the pH of the phosphate solution is raised to 5,

the phosphates precipitated will be, first, ferric, then aluminium, and finally chromium, but if the quantity of phosphoric acid in the solution is inadequate to form any or all of these phosphates, then the acid will combine with the bases in the order in which they are precipitated, and consequently the hydroxides themselves may be precipitated. Hence, by having a quantity of these three bases, and preferably of ferric hydroxide, more than sufficient to combine with the total amount of phosphoric acid present, the phosphate will be completely removed without precipitation of the bases belonging to the subsequent groups. Acetic acid has a marked tendency, owing to the formation of soluble basic acetates, to retain the hydroxides in solution even though the pH's at which they are normally precipitated may have been exceeded (*vide* p. 314). These acetate solutions are, however, completely decomposed on boiling, although long boiling may be necessary if too much acetate be used.

CHAPTER XIX.

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATIONS IN THE ELECTRO-DEPOSITION OF METALS.

BEFORE discussing the necessity for the careful regulation of the hydrogen-ion concentrations of solutions from which certain base metals, such as nickel, cobalt, iron, and manganese, are to be cathodically deposited, it will be an advantage to consider the essential factors on which electrode deposition depends. They are as follow : (1) the relative position of the metal in the electro-chemical series, *i.e.*, its normal electrode potential, and the effect which variations in metal-ion concentration will have upon the actual metal potential set up during deposition, (2) the potential of the hydrogen electrode when immersed in the particular solution, (3) the polarisation produced at the cathode, (4) the hydrogen over-voltage or over-potential, (5) current density ; and (6) the precipitation pH of the hydroxide.

It will be seen from the formula, $E = \epsilon + \dfrac{0\cdot058}{n} \cdot \log c$,

connecting the actual potential difference E, between a metal and the solution, the electrolytic potential ϵ, and the concentration c, of the metallic ions in the solution, that decreasing concentrations of metal-ions below that of one-molar will cause the electrode potential to become increasingly less noble, *i.e.*, more negative, and alternatively more positive for greater concentrations. In order to deposit at the cathode metals more electro-positive than hydrogen—say, copper or silver—from their simple salt solutions, the cathode potential with respect to that of the normal hydrogen electrode will have to be increased slightly above the equilibrium or static potential as calculated from the formula. This excess in potential is due to polarisation, which for noble metals is usually of the order of a few centivolts only, in other words, the deposition takes place in nearly a reversible manner. The metals baser than hydrogen, *i.e.*, more negative, *e.g.*, iron, nickel, cobalt, chromium, and manganese, require considerable polarisation before they can be deposited, and therefore on electrolysis, potentials are required for the cathodic deposition of these

metals which are considerably higher than the calculated equili- brium potentials.

The proximity of the cathode potential to that which would be assumed by a hydrogen electrode, supposing it to behave normally, immersed in the electrolyte, is a matter of some great importance, for on it depends whether metal, or hydrogen, or both, will be discharged at the cathode. Thus, consider an acid solution of copper sulphate containing 1 gram-molecule of cupric ions and 1 gram-molecule of hydrogen-ions in the free acid. Under these conditions the copper potential would be the normal electrode potential, namely, $+$ 0·34 volt and the hydrogen potential 0 volt. For greater acid concentrations the hydrogen potentials would actually become positive, and consequently for such acid solutions there would appear to be a tendency for hydrogen to be discharged before the requisite cathode poten- tial and current density, *i.e.*, the amount of current passed through the cell per unit area of the cathode, usually measured in ampères per square decimetre, had been applied to cause the deposition of the copper. With less acid solutions the hydrogen potential would become negative and thus there would be little risk of hydrogen being discharged. Another factor which would favour the evolu- tion of hydrogen would be for the copper potential to approach the hydrogen potential, as would occur when the copper salt solution became very dilute. It should be mentioned here that another factor—that of hydrogen over-voltage—comes into operation which impedes the discharge of hydrogen at the cathode until a cathode potential is set up more negative than that of the hydrogen electrode. In practice, for electrolytic copper refining a sulphuric acid solution of copper is used containing about 4 per cent. of copper and 10 to 13 per cent. of free sulphuric acid, and the acid and copper contents are continuously maintained at this concentra- tion in order to reduce any loss in current or cathode efficiency through waste of current in the production of hydrogen.

Referring to the base metals, it is found that the great electro- negativeness of magnesium is such that whenever a potential is applied to a cathode in a magnesium salt solution, the current is utilised in discharging hydrogen, thereby depleting the catholyte of its hydrogen-ions and consequently magnesium hydroxide eventually begins to precipitate. This prevents the attainment of the requisite magnesium potential. The reason will be apparent from the chart, Fig. 76, which gives the hydrogen electrode poten- tials for different pH's side by side with the electrolytic potentials of the various metals. The stages at which the various hydroxides begin to be precipitated are also indicated. The gradually in-

creasing concentration of hydroxyl-ions brought about by the evolution of hydrogen in the liquid surrounding the cathode will, though the conditions may also prevail for the metal to be deposited on the cathode, approach that pH when the hydroxide or allied basic salt begins to form. This will make the deposited metal incoherent and spongy through the hydroxide becoming embedded in the crystal structure of the metal, thereby imparting to it a dull dark surface. As this type of deposit often follows the vigorous discharge of hydrogen the sponginess has been attributed solely to the action of the hydrogen in preventing the normal growth of the metallic crystals. Gas evolution does occasionally impair the deposit, giving it an uneven and sometimes streaky appearance, but it is not in itself the real cause of the incoherence of the deposits. The use of dilute solutions and the too rapid passage of the current through the solution, by employing large currents compared with the area of the cathode, are conducive to the evolution of hydrogen instead of the liberation of metal at the cathode. Thus Patterson (*Proc. Univ. Durham Phil. Soc.*, 1912, **4,** 187) has shown that there are conditions under which solutions of salts of iron, nickel, cobalt, zinc, cadmium or manganese can be electrolysed to produce nothing but hydrogen and the respective hydroxides at the cathodes. Much of the hydroxide (or basic salt) though set free from the catholyte can in some cases be prevented from contaminating the deposited metal by

Fig. 76.—Relationship between Normal Electrode Potentials of Metals and Potentials of the Hydrogen Electrode at which their hydroxides begin to be precipitated.

either agitating the solution or employing a rotating cathode.

Wherever possible, electrolytes should be as concentrated as possible and kept slightly acid. This, however, is not always possible as will be seen to be the case with certain base metals, yet zinc in spite of its " baseness " can, under suitable conditions, be deposited from either solutions containing free acid or solutions in which *the acid is immeasurably small, as far as chemical methods are concerned, but which nevertheless require careful control to prevent the simultaneous deposition of zinc hydroxide with the zinc*. Another point should be borne in mind in regard to the effect which current density may have on the nature of the deposit. In general, when a metal can be so deposited a low current density favours the formation of a coarse crystalline non-adherent deposit, the low current density removing the cathode potential only slightly from that when under equilibrium conditions ; but on the contrary, the application of a high current density necessitates a higher cathodic polarisation E.M.F. before deposition can ensue and the greater rate at which deposition can then take place produces a smooth coherent metal composed of fine crystals. The simultaneous liberation of hydrogen with the metal in the case of metals like iron, nickel, and manganese results in the absorption by the deposited metals of some hydrogen which makes them brittle and causes them to have a tendency to peel off and to crack. The hydrogen can be readily driven off by heating.

It is in the electro-deposition of base metals where the very small concentrations of hydrogen-ions make or mar the efficiency of a process. This will be inferred from the proximity of their normal electrode potentials to those potentials which a hydrogen electrode would assume if it were immersed in the solutions when about to precipitate the various hydroxides. (See Fig. 76.) Thus, if base metals, such as cobalt, nickel, cadmuim, and iron, could be deposited reversibly, *i.e.*, at the equilibrium potentials, from their salt solutions, containing say 1 gram-molecule of the respective kations per litre, then it will be seen from Fig. 76 that these potentials are so close to the theoretical potentials required for the reversible discharge of hydrogen and the resulting precipitation of the hydroxide or basic salt, that electrolyses could only be carried out in which varying amounts of current would be wasted in liberating hydrogen, not to mention the deleterious effect which the basic precipitates may have in becoming entangled in the metallic deposits. These precipitations can, however, be avoided by including in the bath certain buffering agents or mixtures which will keep the *p*H below that required for precipitation of the hydroxide, no matter how much hydrogen may be discharged from the catholyte.

The base metals, except zinc, are irreversible and require high polarisations for their deposition, which increase with increasing current density. The discharge of hydrogen at their surfaces can only take place when the potentials of the cathodes are raised appreciably above those which correspond to the equilibrium or static values of the hydrogen electrode immersed in the particular solutions. These may be calculated from the equation $E = 0.058$ log $[H^{\cdot}]$, or simply $E = -0.058 \times pH$, at ordinary temperatures. The magnitude of these differences, *i.e.*, *over-voltages* or *over-potentials*, depend on such factors as (1) the surface of the cathode (2) the temperature, (3) current density. With zinc this hydrogen over-voltage is so great that it is sufficient to prevent the production of hydrogen from acid solutions of zinc salts, despite the
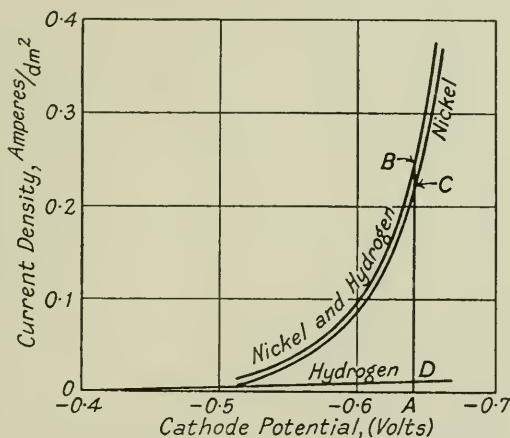
FIG. 77.—Variation in Cathode Potential with Current Density.

fact that the equilibrium-potential of hydrogen is as much as 0.7 volt less negative than that of zinc. In such solutions, however, it is essential to keep the polarisation of the zinc cathode as low as possible and, consequently, relatively small current densities must be used which incidentally restrict the use of the bath as regards its " throwing power," *i.e.*, the even distribution of the deposited metal on the electrode, an essential factor in zinc-plating.

The hydrogen over-voltage for metals of the iron group of metals is at ordinary current densities usually low. As may be seen from Fig. 77, the reversible potential of nickel in a salt solution containing 1 gram-molecule of its ions is less negative than the reversible potential of hydrogen at the pH, 5-6, of ordinary nickel salt solutions, yet nickel deposition is always accompanied by

hydrogen evolution even at small current densities. This is due to the nickel cathode becoming polarised, no doubt through the fact that the cathode becomes composed of a nickel-hydrogen alloy, the potential of which becomes increasingly negative, when either the hydrogen-ion concentration of the solution or the current density is raised (Foerster and Schade, *Z. Elektrochem.*, 1916, **22**, 96). Foerster (*Elektrochemie wässriger Lösungen*, 1922, p. 366) states that for the deposition of nickel from a solution, normal with respect to nickel sulphate and one-hundredth normal with respect to sulphuric acid, at 16° C. with 0·9 ampères per square decimetre the cathode efficiency was as low as 40 per cent., *i.e.*, 60 per cent. of the current was utilised in the generation of hydrogen, whereas the diminution in the polarisation produced by raising the temperature to 50° C. gave an enhanced efficiency of 80 per cent. That hydrogen has a marked effect on the potential of a base metal may be seen from an observation of Smits and Lobry de Bruyn (*Theory of Allotropy*, 1922, p. 327), who found that the potential of nickel free from hydrogen in N-$NiSO_4$ was $-$ 0·194 volt, but changed with time to $-$ 0·35 volt, the potential of the hydrogen electrode in the solution.

In order to deposit base metals from their solutions, it is necessary to employ concentrated metallic salt solutions to keep the cathode potential at which deposition takes place as slightly negative as possible, and to keep the pH of the solution only just below that at which the hydroxide becomes precipitable. This, as may be seen from Fig. 77, will tend to make the hydrogen potential more negative than that of the metal, and coupled with the small hydrogen over-voltage, will enable the metal to be deposited. The differences between the metal- and hydrogen-potentials which generally are small, will cause some hydrogen to be liberated. Its proportion may be considerably reduced by employing a high current density which will also increase the rate of deposition. Another important factor is the maintenance of as large a ratio of the concentrations of metal-ions to hydrogen-ions as possible. The upper curve, given in Fig. 77 (*vide* Haring, *Trans. Amer. Electrochem. Soc.*, 1924, **46**, 110) is typical of the effect produced on the cathode potential by increasing the current density of a nickel plating solution (cathode potentials are measured by joining a calomel half-element in direct contact with the cathode and finding the fall in potential between the two poles in the usual way).

It is seen that nickel did not begin to deposit until the potential of the cathode became more negative than $-$ 0·5 volt ($\epsilon_H = 0$), hydrogen alone being liberated. Thereupon a rapid increase in potential occurred with the increasing current

density. This enabled more and more nickel to be deposited and prevented relatively less and less current being wasted in liberating hydrogen. The curves C and D, which were plotted from the various current efficiencies at the respective current densities and cathode potentials, show what portions of the current densities were utilised in depositing nickel and evolving hydrogen respectively. As the cathode efficiency is the ratio of the metal actually deposited to that which the current would have deposited under ideal conditions, i.e., if no current had been dissipated in producing hydrogen, it will be seen from Fig. 77 that for any particular point, B, say, on the upper curve, the amount of current represented by the ordinate AD was utilised in setting hydrogen free, and that shown by AC the amount used in metal deposition.

The total current (in terms of current density) passed then was equal to AD + AC = AB, and therefore the percentage nickel cathode efficiency was AC/AB × 100. Hence if curves similar to those given in Fig. 77 have once been ascertained for any given electrolysis bath under given conditions the measurement of the cathode discharge potential will constitute a method by which the cathode efficiency can be calculated. As emphasised by Haring, the latter is a most important factor in the " throwing power " of nickel plating baths, in other words, in obtaining baths, which will cause the nickel to be deposited uniformly over the article undergoing plating.

Much of the efficiency depends upon keeping the hydrogen-ion concentration of the bath as low as possible without producing deposits contaminated with basic precipitates. The hydrogen-ion concentration of an electrolysis bath as a whole, depends primarily upon securing equal anode and cathode efficiencies, for if the former becomes less than the latter, the solution will become more acid, and vice versâ. If the acidity of the bath increases, there will be a tendency for the anode to corrode, and thereby to lower the cathode efficiency. The maintenance of a suitable pH can usually be effected by placing in the bath a suitable buffer, one which, as far as the catholyte is concerned, will react with the liberated hydroxyl-ions, and in so doing produces very little change in hydrogen-ion concentration. R. Thompson (*Trans. Amer. Electrochem. Soc.*, 1922, **41, 344**) has investigated the effects of adding boric acid, sodium fluoride, and free hydrofluoric acid to nickel plating baths. His results are given in Fig. 78, which shows the effect on the pH of adding either 0·2 N–H_2SO_4 or 0·2 N–NaOH to 50 c.c., N–$NiSO_4$ containing the " buffers " marked on the diagram. Maximum efficiency was obtained at about pH 6, which is just below that at which the precipitation of nickel hydroxide

begins. The curves show that by using boric acid appreciable amounts of alkali or acid may be added before the acidity is in-
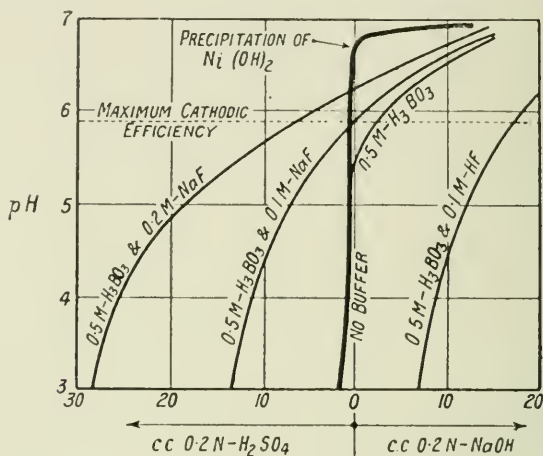
FIG. 78.—The Effect of Buffers on pH of Nickel Plating Solutions (N-NiSO$_4$).

creased by one pH unit. It is often the practice to put ammonium chloride in a nickel plating bath, about 0·25 N, in addition to the boric acid.
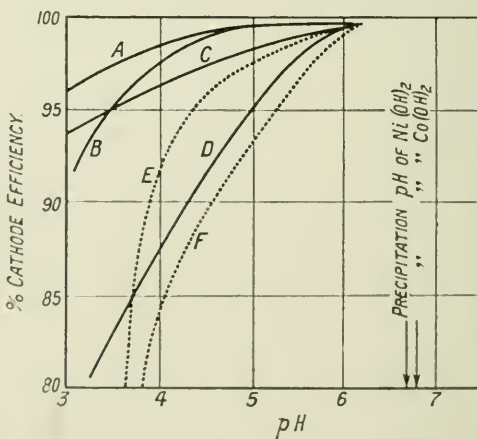
FIG. 79.—Relationship between Cathode Efficiency and pH of Nickel and Cobalt Plating Solutions.

Fig. 79 gives the results of Thompson (*loc. cit.*) and Montillon and Cassel (*Trans. Amer. Electrochem. Soc.*, 1924, **45**, 266) on the

importance of the pH of nickel and cobalt plating baths in pro- moting the greatest efficiency.   Curves A, B, C, and D refer to nickel (Thompson), and E and F to cobalt (Montillon and Cassel). For A and B, the bath was N–$NiSO_4$, o·25 M.–H_3BO_3 and o·1N–NaCl, the current density for A being 1·5 amp./dm² and o·2 amp./dm² for B.   C and D refer to baths containing o·1 N–NaF in place of the sodium chloride, current densities being 1·5 and o·2 amp./dm² respectively.   E and F refer to baths containing 312 grams of cobalt sulphate per litre, 14 grams of sodium fluoride, and boric acid nearly to saturation, the current densities being 3·0 amps. for E, and 5 amps. for F, per square dm. In every case, maximum efficiency, nearly 100 per cent., was ob- tained when the baths were at pH 6, nickel hydroxide precipitating at pH 6·7 and cobalt hydroxide at pH 6·8.   Montillon and Cassel found that nickel plating carried out at pH 6 resulted in a very dense, greyish-white, adherent smooth surface having no gas streaks or pits.   At pH 4·5 the plating was fairly good, though it had a few gas streaks, but at pH 3·5 there were many gas streaks, and the deposit tended to peel off.   In cobalt work, the plating was excellent at pH 6, but became unsatisfactory below pH 4·5.   Thompson states that nickel deposits show evidence of blistering, cracking, and curling when obtained from a bath at pH 6·3 to 6·5.

More recently, Foerster and Krüger (*Z. Elektrochem.*, 1927, **33,** 406) have investigated the electrolysis of nickel sulphate solu- tions containing varying amounts of nickel chloride and 2 per cent. of boric acid between nickel electrodes at 20° C., and in order to ascertain the best practical conditions for the electro-deposition of nickel observed the different bath voltages, anode potentials, both the anodic and cathodic efficiencies and the pH values.   As the efficiency of the electrolysis as a whole depends upon the efficiencies of the two poles, namely that the rate of dissolution of the anode should be equal to that of the nickel deposition on the cathode, it is essential to avoid the anode acquiring a passive state, which ap- parently can be done by including in the bath sufficient nickel chloride.   This enables the chloride-ions to interact with the peroxide film which in covering the anode produces a condition of " temporary passivity."   By employing a low current density, or keeping the chloride concentration high, they found that the anode could be kept active continuously and dissolved with high current efficiency between potentials + o·40 and + o·58, the potential of the normal hydrogen electrode being taken as zero, where the pH of the electrolyte gradually became higher.   Good cathodic deposits were obtained at pH values below 5·5, which are somewhat lower than those found by previous workers.   Foerster   and

Krüger also found that high pH values lead to flaking and cracking through the development of hydroxide precipitate within the metal, and which thereby enables bubbles of hydrogen to adhere and so to cause pitting.

Zinc has been deposited from a zinc sulphate solution containing partly neutralised acetic acid as the buffering agent, but quite recently Thompson (*Trans. Amer. Electrochem. Soc.*, 1926, **50**, 219), has called attention to the fact that acid zinc plating baths have low " throwing power " and that higher current densities could be employed if the plating were carried out from zinc chloride or sulphate solutions of about 2 N, and being 3 to 4 N with respect to either sodium or ammonium chloride and 0·25 N —with respect to either aluminium chloride or sulphate. He was able to use 5 amps./dm² with stationary cathodes and up to 15 amp./dm² with moving cathodes. Partly neutralised acetic acid could also be used in place of the aluminium salt. Table 80 on page 278 shows that zinc hydroxide precipitates at pH 5·2, whereas aluminium hydroxide does so at pH 4·2 from sulphate solutions, though from chloride solutions actual precipitation is usually delayed until higher pH's are obtained (Britton, *J. Chem. Soc.*, 1927, 423). Thompson found boric acid to be useless, as would be expected from its great weakness, and he adds that though the aluminium salt in behaving as a buffer might cause aluminium hydroxide to separate, the presence of the hydroxide had no deleterious effect on the plating. The appearance of a precipitate, moreover, gave a clue of the pH of the bath and it also tended to protect the anode from attack. Aluminium salts appear to have been used in zinc plating baths first in 1854. The cathode efficiency may by their use become nearly 100 per cent.

The electro-deposition of iron has not yet gained very great technical importance though it was used during the war for restoring worn aircraft parts. Bouchayer and Viallet and Grenoble in France manufacture boiler tubes in this way. W. E. Hughes (*Trans. Amer. Electrochem. Soc.*, 1921, **40**, 185) gives a complete summary of the baths which have been employed, some of which contain ammonium salts as buffers, whereas in others, particularly in ferrous chloride solutions, a little acid is included. It appears that the ferrous sulphate baths should contain only a very small amount of free acid, for too much acid reduces the cathode efficiency in a marked manner, whereas chloride baths should be neutral. The ratio $[Fe^{\cdot\cdot}]/[H^{\cdot}]$ must be large and the deposition carried out at an elevated temperature.

The electro-deposition of manganese has received some attention in recent years, particularly by Grube and Metzer (*Z. Elec-*

trochem., 1923, **29,** 17, 100) and Allmand and Campbell (*Trans. Faraday Soc.*, 1924, **19,** 559 ; 1925, **20,** 379). Bunsen obtained electrolytic manganese from manganous chloride solution as early as 1854. Grube and Metzer using baths of 6-7 N-$MnCl_2$, 1·5 N-NH_4Cl and 0·1 N-HCl with a current density of 20 amp./dm^2 obtained a current efficiency of 50-60 per cent. Allmand and Campbell obtained lower efficiencies, but they secured their best results when the pH lay between 6 and 8. When 0·36 per cent., or more H_2SO_4 was present in the catholyte the manganese deposition ceased. A perusal of Fig. 76 will make the fact that manganese can be deposited electrolytically appear surprising, but it must be stated that the baseness of manganese is somewhat compensated for by its high hydrogen over-voltage. Whether the electro-deposition of manganese can be made an economic success remains a question of doubt.

Effect of Gelatin on Electro-deposition.

" Addition agents," usually of an organic colloidal nature, are sometimes employed in electrolysis baths for the purpose of improving the physical character of the deposited metal and sometimes to facilitate deposition. Thus Mathers and McKinney (*Trans. Amer. Electrochem. Soc.*, 1915, **27,** 131) recommend the addition of Barbadoes aloes to electrolytes containing lead nitrate and acetic acid in order to obtain satisfactory even deposits, and in the Betts Process for the Electrolytic Refining of Lead (*Trans. Amer. Electrochem. Soc.*, 1905, **8,** 64) in which the bath is composed of a solution of lead in hydrofluosilicic acid, gelatin in the form of glue is included which causes a slight increase in the polarisation of the cathode and thus increases the cathode efficiency together with the formation of a smooth deposit. Gelatin has also been observed to raise the cathode potential when copper is being deposited from acid solutions (Le Blanc, *Electromotorische Krafte der Polarisation, Halle*, 1910 ; E. Müller and Bahntje, *Z. Elektrochemie*, 1906, **12,** 317 ; Siewerts and Wippelmann, *Z. anorg. Chem.*, 1915, **91,** 1). This increase in polarisation is also reflected in the change in the texture of metallic deposits obtained, especially in the production of more dense and smooth, fine-grained metal. Pring and Tainton (*J. Chem. Soc.*, 1914, **105,** 710) found that the efficiency was enhanced by the addition of gelatin in the deposition of zinc from a strongly acid electrolyte using a very high current density of 20-100 ampères per square decimetre. W. E. Hughes (*The Metal Industry (London)*, 1924, **25,** 269), however, found that in the electrolysis of zinc sulphate solutions gelatin

had practically no effect upon the structure of the deposit, but that it had a marked effect when the solution was acidified with sulphuric acid. The former solutions were alkaline to Congo red, *i.e.*, $pH > 4$, and the latter acid, *i.e.*, $pH < 4$. It appears, therefore, that under certain conditions of acidity the use of gelatin or glue gives rise to improved deposits, though it should be mentioned that Mathers (*Trans. Amer. Electrochem. Soc.*, 1924, **46**, 84) claims to have found no improvement in the tin deposited from tin silico-fluoride bath containing glue.

Frölich (*Trans. Amer. Electrochem. Soc.*, 1924, **46**, 67) has directed attention to the fact that in general it is only when the gelatin is added to an electrolyte of high hydrogen-ion concentration that the gelatin is found to have a beneficial effect. This, he argues, is in harmony with the amphoteric nature of gelatine, its isoelectric point being at pH 4·7. Thus in acid solutions gelatin is found to combine with the acid forming salts and therefore, when the solution is subjected to electrolysis, the gelatin migrates towards the cathode where it accumulates and offers additional resistance to the transportation of the inorganic cations up to the cathode surface. This increases the cathodic polarisation. It is highly probable that in ordinary electro-depositions the pH of the film of solution directly in contact with the surface of the electrode is different from that of the main body of the solution. Thompson (*Trans. Amer. Electrochem. Soc.*, 1922, **41**, 333) states that this is the case in the deposition of nickel from an acid electrolyte, and Eiffe (*Thesis, Massachusetts Institute of Technology*, 1924) cited by Frölich, has observed in zinc deposition experiments that for a certain zinc salt concentration a pH close to 6·2 existed next to the cathode whereas the acidity of the electrolyte varied as widely as from pH 6·2 to pH 2·5. That a gelatin film is formed on the cathode may, as Frolich states, be inferred from the increase in the size of the gas bubbles which emerge from the cathode and the difficulty with which they break loose and escape. Moreover, in acid electrolytes gelatin has no effect on the anode. As the pH of gelatin decreases from 4·7, the swelling in water increases until pH 3·2 is attained after which the swelling becomes less again. Hence the density of the cathodic film of gelatin, and consequently the impeding effect which it will have on the maintenance by diffusion and convection of a high concentration of electrolyte immediately around the cathode, will depend upon the local pH. Blum and Rawdon (*Trans. Amer. Electrochem. Soc.*, 1923, **44**, 397) state that coarse crystalline deposits of metals are produced by having an excess of metal-ions in the catholyte, whereas low metal-ion concentrations with a large reserve of

undissociated salt, *e.g.*, complex cyanides, are conducive to the formation of smooth, fine-grained deposits. Frölich suggests that the latter conditions exist when the cathode is closely surrounded by a film of gel of high viscosity, for its presence restricts considerably the passage of the electrolyte to the cathode surface except those cations which are in the act of being deposited. If too much gelatin be used and the pH of the cathode film be such as to make the gelatin deposited therein dense, it is conceivable that circumstances may arise when the resistance encountered by the cations on the point of being deposited becoming so great as to force the metal to deposit within the gelatin film itself. Some little co-precipitation of gelatin with the copper takes place from acid copper baths and in practice it is necessary to add fresh quantities of gelatin from time to time. Frölich is of the opinion that while the introduction of gelatin into the deposit certainly affects its appearance, co-precipitation is not essential in order to improve the texture of the deposited metal. The low acidities of the cathode liquid films in the case of zinc and nickel, usually of pH greater than 4·7, prevent the formation of gelatin layers on the cathode, the gelatin migrating to the anode, and so the gelatin is without any appreciable effect on the deposited metal. When acid solutions are used the gelatin may become entangled in the deposit. The deposits from solutions of low acidity have in some cases been found to contain organic matter, probably as the result of the catalytic reduction of the gelatin at the surface of the electrode.

CHAPTER XX.

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATIONS IN THE PRELIMINARY STAGES OF LEATHER MANUFACTURE.

In this chapter an attempt is made to show how the efficiency of many reactions, to which the proteins present in skins have to be subjected before the skins are ready for tanning, depends upon the hydrogen-ion concentrations in the various liquors, such as those employed for " soaking," " liming," " bating " and " deliming," " pickling " and " drenching." The developments in biochemical research have shown that in order to secure (or to avoid) the optimum activity of the enzymes and bacteria involved in leather manufacture specific ranges of hydrogen-ion concentrations have to be established.

Epitome of Stages of Leather Manufacture.

It will be an advantage to give at the outset a short *résumé* of the stages through which a skin has to pass in order that it may become an imputresible, pliable, and durable leather. Before the skins are actually tanned, they have to undergo several treatments, so that all possibilities of putrefaction are eliminated, and also that the fibres are in the best condition to receive the tannage. These treatments comprise the " preservation," and, when necessary, the " disinfection " of the skin, " soaking and fleshing," in which all adipose tissue and adhering flesh are removed, and the skins receive a general trimming which involves the removal of ears, cheeks, hoofs, and tails. One of the objects of soaking, besides to facilitate " fleshing," is to render the skins free from soluble globulins and proteins. The next stage is that of " unhairing and scudding," in which the hair is first loosened from the skin, which may be effected by a variety of methods, and then it is mechanically removed or scraped off with a blunt and somewhat curved two-handled knife on a sloping rounded " beam " of wood or metal. The commonest method of removing the hair and the epidermal layer now used is that known as " liming " in a saturated solution of slaked lime, until the hair and epidermis have become so loose that they may be rubbed off with very little difficulty. The alkaline solution also

has the effect of causing the skin to swell or " to undergo plump-
ing," due to the imbibition of water. The skin, however, is not
yet in a condition suitable for tanning, for the bundles of fibres
in the skin, although more or less separated through the swelling
of the skin, are held together by elastic protein fibres, the chief
protein being " elastin." Again, the skin is somewhat impervious
to liquors in its now rubbery or plump state, and consequently
before the absorption of tanning liquors becomes possible the
skin must be subjected to yet another important treatment to
remove the undesirable proteins, such as " elastin," and at the
same time to diminish its bulk or swelling ; in technical terms to
bring about " falling." This process is that of " bating," and
originally consisted in keeping the unhaired skins in a warm infusion
of hen or pigeon dung, or in the case of light skins, of dog dung
when it was called " puering," until they had become extremely
relaxed and flaccid, or fallen, and became so soft as to retain the
impression of the thumb and finger, and sufficiently porous that
air could be forced through them. This objectionable and filthy
process is gradually being superseded by the use of the trypstic
ferments or enzymes present in drugs, chiefly pancreatin, obtained
from the pancreas of animals, in conjunction with ammonium
chloride as the deliming agent. In the older process the deliming
agent was the weak organic acids liberated by the decomposition
of elastin by the enzyme action. Before finally subjecting the
skin to the tanning liquors,. it is usually either " drenched " or
" pickled," the former being preferable if vegetable tanning liquors
are to be subsequently used, and the latter if chrome liquors ; in
fact, pickling prior to chrome tanning is almost imperative.

    " Drenching," which may sometimes take the place of bating,
is carried out by placing the skin in a liquor at 30° to 35° C.,
containing 5 to 10 gms. of bran per litre and allowing fermentation
to ensue. Gases, such as carbon dioxide, hydrogen and nitrogen
are evolved, and also organic acids—e.g., formic, acetic, butyric,
and lactic acids, are produced which render the skins acidic in
reaction. Under certain conditions this may be very beneficial,
but as the treatment is of a somewhat uncertain character, careful
control is necessary, and also care must be taken to ensure that the
skins do not get damaged by the formation of gases inside the skin
which in forcing their way through the grain surface make per-
forations. Too high a temperature and especially if too much
acid is formed, may also cause some of the chief protein, collagen,
in the skin to decompose and to give an unsatisfactory spongy
leather. Organic acids and sometimes hydrochloric acid, are often
used in place of bran liquors.

" Pickling " is often resorted to when the skins are not to be tanned immediately, and also when they are to be chrome tanned. It used to be the practice to treat the skins, limed or bated, with a dilute solution of sulphuric acid until the desired amount of swelling had been obtained, and then to repress the swelling somewhat by immersion in a saturated brine solution. Nowadays, pickling can easily be controlled chemically, merely by titration to methyl orange, and one pickling solution, therefore, is used often containing very dilute sulphuric acid and sodium chloride to the extent of about 1 mol. per litre. The object of both " drenching " and " pickling " appears to be to bring the acidity of the skins to the reaction most convenient for efficient tanning, and as will be shown later, the proper adjustment of acidity is a question of considerable importance in tanning.

The process of tanning was formerly carried out entirely by means of aqueous extracts of tanning derivatives obtained from various barks. Oak bark extracts are preferred on account of the firmness and solid nature of the resulting leather, though hemlock bark finds great favour in America for the manufacture of heavy leather. For sole leather the tannins of chestnut and oak woods are often used in conjunction with other substances. Care must also be exercised to use only those tannin extracts from which the tannin will not be precipitated when the skins are placed in them, such as would happen if an unsatisfactorily delimed skin were immersed in a quebracho extract. Another important, and, indeed, a very valuable means of tanning light skins in particular, is by means of basic chrome liquors, a process which will be discussed fully in Chapter XXI. After tanning, the leathers are subjected to various finishing operations, such as neutralising, fat-liquoring, dyeing, and in the case of chrome-tanned leather some type of filling will be necessary to compensate for the so-called " emptiness."

Collagen and Gelatin.

Having outlined the various stages of leather manufacture, we shall now devote our attention to the physical chemistry of the subject, so that, when reviewing the several treatments in greater detail, we shall be able to get a better insight into the reasons for the various procedures and, moreover, to see why a rigid regulation of the hydrogen-ion concentrations of the solutions furnishes an excellent method of controlling the whole process of manufacture. There seems to be little doubt that the application to leather manufacture of the conception of acidity and alkalinity as due to the

variation in the concentration of hydrogen-ions, and the methods of measuring these concentrations, have marked one of the greatest advances made in leather chemistry.

Skin comprises several proteins. Collagen is the most important constituent of the derma, being the protein in the white fibres of the connective tissue. It is these fibres which determine the quality of leather which can be produced. The keratins are found in the epidermis, and the hair or wool ; the mucins, albumins, and globulins in small amounts in the derma ; and elastin in the yellow elastic fibres. Other proteins are also present in the derma, but they have not hitherto received names. All these types of proteins, with the exception of collagen and some of the unidentified proteins, are eliminated in the processes prior to tanning ; thus the albumins disappear on treatment with water, they alone being soluble, the globulins are soluble in dilute sodium chloride solutions, the mucins in dilute alkaline solution, the keratins though soluble only in strongly alkaline solution are largely removed mechanically, after the appropriate putrefactive fermentation has been allowed to take place, and the elastin by digestion with trypsin. According to Thomas and F. L. Seymour-Jones (*J. Amer. Chem. Soc.*, 1923, **45,** 515) collagen is also attacked by trypsin when the action is allowed to take place at 40° C. at pH 5·9, but the amount of collagen which becomes soluble in the bating or modified bating processes is generally very small. Collagen, in the form of Hide Powder, can be prepared from skin in the laboratory by a method parallel to that used in preparing the skin for tanning. The skin is prepared by cutting extraneous tissue away, after which it is thoroughly washed and the soluble proteins extracted with several changes of 10 per cent. sodium chloride solution in a shaking machine. The hair and epidermis is now loosened by immersing in a saturated solution of slaked lime containing about 0·1 per cent. sodium sulphide for several days with frequent agitation, and when sufficiently loose the hair and outer skin is scraped away with a knife. This exposes the grain surface which is then removed. After the lime has been extracted by washing, the elastin fibres may be dissolved out by digestion at 40° C. with pancreatin solution containing 1 gm. per litre and which has been suitably buffered to the pH value of bating liquor, *viz.*, *ca.* pH 7. Wilson (*The Chemistry of Leather Manufacture*, 1923, p. 72) gives 2·8 gm. NaH_2PO_4 and 18 c.c. N–NaOH per litre, which on calculation is found to give a pH of 7·4. After cutting up into small pieces the skin is soaked in water and treated with hydrochloric acid until faintly acid to methyl orange and washed first in running water, then with alcohol and finally

with xylene, after which it is air-dried and crushed to a fibrous powder.

Upon prolonged heating at about 70° C. with water collagen passes into gelatin, though the nature of the change which takes place is still a question of doubt. Hofmeister (*Zeitsch. physiol. Chem.*, 1878, **2**, 299) held that it was one of dehydration and that gelatin was the anhydride of collagen, whereas Emmett and Gies (*J. Biol. Chem.*, 1907, **3**, 33) suggested it was a case of intramolecular rearrangement. As pointed out by later workers there is good evidence in support of both contentions. Much of the waste skin of the tannery is converted into gelatin or into the more crude form of glue. Bogue (*Ind. Eng. Chem.*, 1923, **15**, 1154) has studied the conversion of collagen into gelatin with respect to ranges of pH which should be maintained during boiling. He found that the pH should be kept either between 3 and 4 or 7·5 and 8·5. Between pH 4·5–6·0 the hydrolytic reaction proceeds too slowly, while at values below 3 or above 8·5 the gelatin, which is formed, rapidly breaks down. It is best to use about 12 parts of water to each part of dry collagen and to keep the temperature at 80° C. for about 8 hours. The previous swelling of the stock may best be carried out with lime or lactic acid, but excess of reagent must be removed before heating. Bogue favours the view that collagen is not a simple anhydride of gelatin but rather a product of chemical condensation.

The analytical data given in Table 88 show that collagen, as

TABLE 88.

COMPOSITION OF COLLAGEN.

Skin.					Per Cent. C.	Per Cent. H.	Per Cent. N.	Per Cent. O.
Ox (average)	.	.	.	.	50·5	6·5	17·8	25·2
Calf	.	.	.	.	50·2	6·5	17·8	25·5
Camel	.	.	.	.	50·0	6·4	17·7	25·9
Horse .	.	.	.	.	50·2	6·4	17·9	25·5
Pig	.	.	.	.	49·9	6·3	17·8	26·0
Rhinoceros (average)	.	.	.	50·2	6·4	18·0	25·4
Goat	.	.	.	.	50·3	6·4	17·5	24·8
Deer	.	.	.	.	50·3	6·4	17·4	25·9
Sheep	.	.	.	.	50·2	6·5	17·1	26·2
Chamois	.	.	.	.	50·1	6·4	17·3	26·2
Dog	.	.	.	.	50·3	6·5	17·0	26·2
Cat	.	.	.	.	51·1	6·5	17·1	25·3

derived from various animal skins, is of a fairly constant composition. The figures were taken from a paper by von Schroeder and Pässler (*Dingl. polytech. J.*, 1893, **11-13**, 287) and refer to water-free products.

The composition of collagen bears a striking similarity to that of gelatin. Table 89 gives typical analyses of gelatin. It does not, however, give the sulphur content, which is always very small.

TABLE 89.

COMPOSITION OF GELATIN.

Per Cent. C.	Per Cent. H.	Per Cent. N.	Per Cent. O.	Chemist.
49·9	6·4	17·7	26·0	Rakusin, 1922.
50·0	6·5	17·5	26·0	Fremy, 1854.
50·0	6·7	18·3	25·0	Schutzenberger, 1876.

Of the recorded analyses since 1843, the mean nitrogen content of gelatin is found to be 18 per cent.

Attention has specially been directed to the relationship which subsists between collagen and gelatin, for the latter substance, being easier to experiment upon, has received much more attention. Its importance from the point of view of leather chemistry is great, inasmuch as it has many properties and reactions in common with collagen. This is true with regard to their behaviour towards tanning agents, and towards both acids and alkalis. The application of the results of physico-chemical researches on gelatin to the chemistry of leather has thrown much light on many of the processes, and for this reason we shall now pay some attention to them. Hardy showed in 1899 that proteins are soluble in acids and then become positively charged, whereas in alkalis they dissolve but become negatively charged. At some intermediate stage when they carry no electric charge, a point is reached which he called the " isoelectric point," when they also possess minimum solubility. The location of the isoelectric point, though formerly a matter of academic interest, has now become a subject of technical importance, and with the development and application of potentiometric methods, it has become an easy matter to ascertain the pH corresponding to the isoelectric point. From a qualitative point of view, proteins may be considered as complex amino-acids, thus $R\Big\langle{\substack{COOH,\\NH_2}}$, and therefore react with acids in solutions more acid than that of the isoelectric point as bases, e.g., $HOOC . R . NH_2 + HCl \rightarrow HOOC . R . NH_2 . HCl$; and with bases in solution more alkaline than that of the isoelectric point, e.g.,

$$NH_2 . R . COOH + NaOH \rightarrow NH_2 . R . COONa + H_2O.$$
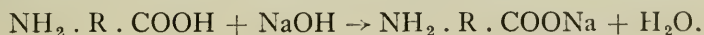
Gelatin, however, does not react with a definite amount of either acid or alkali. The amounts depend upon the pH of the solution and the previous treatment of the gelatin (*cf.* Lloyd and Mayes, *Proc. Roy. Soc.*, *B.*, 1922, **93**, 69 ; Hitchcock, *J. Gen. Physiol.*, 1921-2, **4**, 733 ; Atkin and Douglas, *J.I.S. Leather Trades Chemists*, 1924, **8**, 584). The author carried out some potentiometric titrations on gelatin solutions which had undergone certain previous treatments, and in view of their interest here in showing the course of the reactions into which gelatin may enter, and incidentally as they throw some light on the reaction which gelatin undergoes when subjected by protracted heating with water, when it is found that the resulting gelatin thereby loses its power of gelatinisation and therefore becomes useless for adhesive purposes, reference will now be made to the results obtained.

Hydrogen Electrode Titrations of Gelatin.

In recent years it has been realised that gelatin prepared by heating either collagen or ossein with water contains some decomposition products and therefore requires purification. Thus Sheppard, Sweet, and Benedict (*J. Amer. Chem. Soc.*, 1922, **44**, 1858) purified gelatin by electrolysing the jelly and precipitating the gelatin from it with acetone. The gelatin used by the author was purified by the method described by Knaggs and Schryver (*Biochem. J.*, 1924, **18**, 1079), which is one of electrodialysis of a gelatin solution through a collodion membrane until the gelatin becomes flocculated when it is redissolved and reflocculated until the nitrogen content of the supernatant liquid becomes extremely small. In this way a gelatin was obtained free from electrolytes and also from soluble nitrogenous contaminants.

Solutions (1 gm. in 100 c.c. water) of this product had a pH lying between 4·7-4·8. In one case 100 c.c. were titrated electrometrically using the hydrogen electrode with 30 c.c. N/10–HCl, and then back-titrated with N/10–NaOH at 20° C. The back-titration curve obtained is shown in Fig. 80, marked " purified." Another 100 c.c. of 1 per cent. purified gelatin solution was boiled under a reflux condenser for 24 hours, cooled to 20°, 30 c.c. N/10 HCl added, and similarly titrated. The curve obtained is labelled " boiled." Another NaOH titration was carried out on a 1 per cent. solution of Coignet's " Gold Label " gelatin, containing the same amount of HCl, and the curve obtained is labelled " ordinary." Fig. 80 also contains for the purpose of comparison, the titration curve of 130 c.c. of a hydrochloric acid solution, containing 30 c.c. N/10–HCl, with N/10–NaOH. The position

of the gelatin curves corresponding to its reaction as a base in forming gelatin chloride show that as far as the basic groups in gelatin are concerned there appears to be very little difference, if any, between the gelatins in the three solutions. The figures placed between the HCl and gelatin curves give the number of cubic centimetres of N/10–HCl which reacted with 1 gram of gelatin at the various pH's, and are simply the differences between the amount of hydrochloric acid actually added to the gelatin to give any particular pH and the amount of hydrochloric acid re-
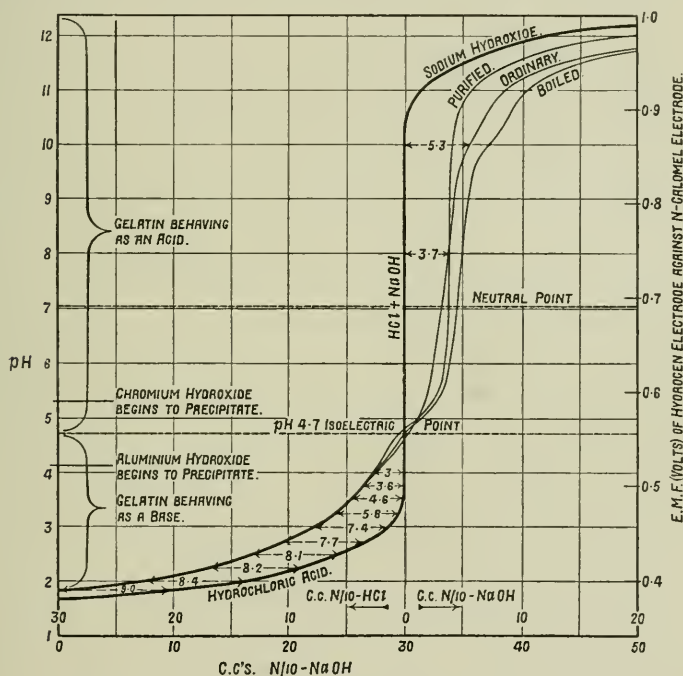
FIG. 80.—Hydrogen Electrode Titration Curves of Gelatin.

quired alone to give the same pH, the unhydrolysed gelatin chloride being taken as neutral. Thus it is seen that in the dilution used at pH 2, 1 gram of gelatin combined with 8·4 c.c. N/10–HCl; at pH 2·5, 8·1 c.c.; at pH 3, 7·4 c.c.; and thereafter the amount rapidly fell off to pH 4·7, the isoelectric point, when it became zero. Similar observations have been made by Loeb (*J. Gen. Physiol.*, 1920-1, **3**, 100), Hitchcock, Lloyd and Mayes, and Atkins and Douglas. Atkins and Campos (*J. I. Soc. Leather Trades Chemists*, 1924, **8**, 408; *J. Amer. L.C. Assoc.*, 1924, **19**, 498) titrated hide

powder by means of indicators and showed that it too, below the isoelectric point, combines with acids in amounts depending upon the pH finally set up.

The remaining parts of the curves given in Fig. 80 indicate the nature of the reactions of gelatin as an acid. The figures give the number of c.c. of N/10–NaOH, which united with 1 gram of gelatin in forming sodium gelatinate. At pH 8, 3·7 c.c. of alkali had combined and at pH 10, 5·3 c.c. Greater amounts of alkali were required in the case of gelatin, which had undergone protracted boiling. It will be observed that the curve corresponding to purified gelatin shows no inflexion between pH 10-11, whereas the other two do, the inflexion being more pronounced in the case of the gelatin which had been boiled. It has long been known that gelatin if heated for a length of time above 37° C., gradually passes into a form which has not the power of forming a jelly and its solutions have diminished viscosities. The transition is more rapid the higher the temperature. It is therefore essential in glue and gelatin manufacture to avoid this change taking place as much as possible. The smooth and inflected curves thus obtained account for the different forms of titration curves obtained by previous workers. The presence of the inflexion appears to be accounted for by some decomposition having taken place, liberating more carboxyl groups, and the fact that the solution prepared from Coignet's gelatin showed the inflexion suggests that it, too, must have contained some decomposition product, probably due to too long heating during the process of its manufacture. According to Thimann (private communication) he has been able to show that the effect of heating gelatin is to produce a soluble form, the transition into which being partly irreversible. Commercial gelatins contain varying proportions of this soluble product, in addition to peptones and other breakdown products. It is interesting to notice that this observation of the author with gelatin is similar to that of Komatsu and Okinaka (*Bull. Chem. Soc.*, Japan, 1926, **1,** 151) in connexion with their studies of the action of superheated water at 120° C. on insoluble proteins, such as edestin, gliadin, and casein. They found that portions thereby became soluble which on titration with sodium hydroxide gave these peculiar inflexions, the magnitude of which depended upon the length of time of heating.

Swelling of Gelatin and the Plumping of Hides.

If gelatin be immersed in solutions of different pH values, it is found that when immersed in solutions at the isoelectric point,

viz., pH 4·7, they undergo the minimum swelling. Miss Lloyd (*Biochem. Jour.*, 1920, **14,** 147) has investigated the swelling of gelatin in leaf-form by finding the increase in weight per each gram of gelatin. Her results, together with those of Sweet (*vide* Sheppard, *Ind. Eng. Chem.*, 1922, **14,** 1025) are given as broken lines in Fig. 81, the appropriate ordinate being given on the right-hand side. It will be observed that on the acid side of pH 4·7 both curves showed a considerable absorption of water occurred from solutions, reaching a maximum value in solutions at pH 2·5-2·6. A more gradual swelling occurred on the alkaline side of the isoelectric point.

The isoelectric point of collagen, in the form of hide powder, has been determined. Thomas and Kelly (*J. Amer. Chem. Soc.*, 1922, **44,** 195) obtained a value of pH 5 by means of acid and basic dyes. E. C. Porter (*J.I. Soc. Leather Trades Chemists*, 1921, **5,** 259), however, arrived at a value of pH 4·8 as being the point which caused the minimum swelling of hide powder. The same value, pH 4·7-4·8, is indicated by the titration curves of Atkin and Campos (*loc. cit.*). It should be mentioned that Porter found points of maximum swelling at pH 2·4 and 12·5. Hence it appears that there is a very close similarity in the physical chemistry of gelatin and its precursor, collagen, and therefore it would be expected that there would exist a close analogy between the plumping of hides and the swelling of gelatin. Fig. 81 gives curves which correspond to the plumping of calf skin as determined by Wilson and Gallun (*Ind. Eng. Chem.*, 1923, **15,** 376) by means of thickness gauge in which a plunger having a circular base 1 square centimetre in area and capable of pressing on the skin under constant pressure (*cf.* Wood, Sand, and Law, *J. Soc. Chem. Ind.*, 1912, **31,** 210 ; 1913, **32,** 398), and to the plumping of cow-hide butt by Page and Gilman (*Ind. Eng. Chem.*, 1927, **19,** 251) using a similar method. The latter chemists aimed at following more closely the changes in plumping under actual tannery conditions by using hide which has been soaked, limed, unhaired and fleshed as the standard instead of hide which had only been bated. Page and Gilman's data showing the variation in pH with the amount of acid (hydrochloric, sulphuric, and lactic) added to hide compare with those given in Fig. 81 for gelatin. The experiments of E. C. Porter (*loc. cit.*) on the swelling of hide powder in solutions of varying pH values are of interest in that they also show that there is a close relationship between the swelling of collagen and of gelatin. He found the volume of hide powder, which had been ground such that it passed through a " 30 " mesh sieve (*i.e.*, a sieve having 30 strands of wire per linear inch) but was

retained by a " 60 " sieve, when allowed to swell in different buffer solutions. For this purpose he took o·5 gram of hide powder and immersed it in 250 c.c. of solution, and after placing in a thermostat for 48 hours with frequent shaking he measured the volume of the swollen powder which had settled down. Such a
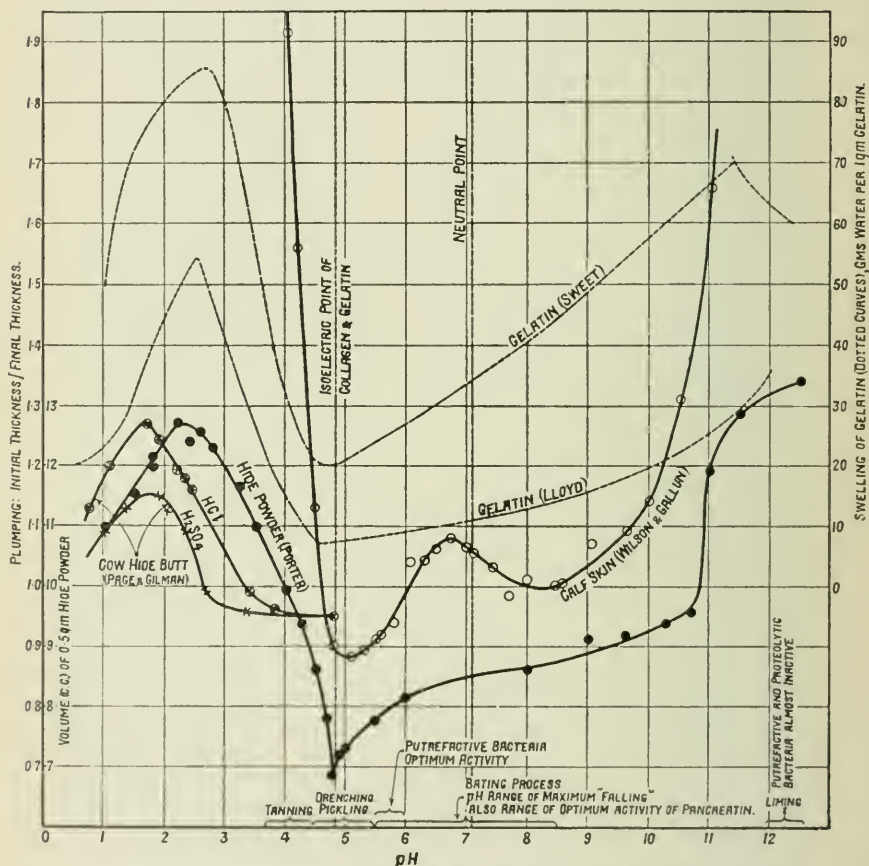
FIG. 81.—Variation in the Degree of Plumping of Hides with the pH of Plumping Liquors ; also Variation in the Swelling of Gelatin Immersed in Solutions of different pH Values.

volume does not represent the true one since a considerable proportion of solution must have been included between the swollen particles, but for comparative purposes this, Porter states, is of no importance. In order to have some check on the repressing effect on the swelling, neutral salts were kept as far as was possible a

at a constant concentration.   R. E. Porter (*J. Amer. Leather Chem. Assoc.*, 1925, **20**, 282) has also studied the plumping of split and unsplit cow-hide.   Page and Gilman suggest that the reason why the maximum plumping occurred at pH 1·8, instead of at a higher pH as in the case of gelatin, is to be found in the fact the pH actually recorded in the hide experiments was that of the external liquor, which most probably was much higher than that which ruled in the interior of the hide.   It appears, therefore, that the cause of swelling is in some way related with the reactivity of gelatin or collagen as either a base or an acid.   It is true that swelling can be repressed by the addition of neutral salts to the bath, which is probably best accounted for by the Procter-Wilson application of the Donnan theory of membrane equilibria and not by any suppression of the ionisation of the gelatin salts (Procter and Wilson, *J. Chem. Soc.*, 1916, **109,** 307).

We shall now consider the chief instances in which hydrogen-ion concentrations provide some means of control of certain stages of leather manufacture.   One of the methods used for the pre-servation of sheep skins, in particular, before de-woolling is to pickle them in solution of a mineral acid (about $N/20$, either HCl or H_2SO_4) containing salt to the extent of 2 N.   It is essential to regulate the plumping which will be caused by the acid and also to be careful to remove the acid before proceeding to tan.   Pickled sheep skins are often chrome tanned without any further treat-ment.   Much of the plumping can be reduced by washing the pickled skins with concentrated brine.   Sometimes skins which come from infected areas (anthrax, foot-and-mouth disease, and rinderpest) require disinfection, and the use of acids in the disin-fecting solutions introduces difficulties.   A. Seymour-Jones (1910) advocated a method for the eradication of anthrax by immersing the dried skins before transportation from 1 to 3 days in a 1 per cent. solution of formic acid and 0·02 per cent. of mercuric chloride.   The swelling is afterwards repressed by soaking the skins for an hour in a saturated solution of common salt.   Another method is that of Schattenfroh (*Collegium*, 1911, 248), who disin-fects with a 2 per cent. HCl and 10 per cent. NaCl solution at 40° C. for three days.   In both cases the acid will tend to plump the skins though this will be largely prevented by the brine.

Except in the case of sheep skins, when de-woolling is carried out from skins which have been treated with acid, the most usual way is to prepare them for unhairing by soaking in alkaline solu-tions.   Here great care must be exercised, for if a liquor be used having too high a pH it may cause considerable damage to both the skins and the hair.   Alkali, however, has the advantage that

in causing some little decomposition to take place around the roots
of the hairs ammonia is produced which causes the hair to become
loose. Sodium sulphide solutions are often used for this purpose,
no doubt due to the buffering effect which sodium sulphide has
on the pH in keeping it below that prevailing in free alkali solutions.
When caustic soda solutions are used for the preliminary soaking
it is essential to use only that concentration which will just promote
swelling and at the same time impart to the liquor a reaction of
about pH 9-10. After swelling has once been begun the skins are
brought to the condition they were in before drying by soaking
in water. Contrary to the opinion of many, the presence of some
little salt in the skin is not deleterious to the subsequent liming
process. In fact, it appears to be an advantage, for as shown by
Harned (*J. Amer. Chem. Soc.*, 1915, **37,** 2460) and Britton (*J. Chem. Soc.*, 1926, 142) neutral salts tend to lower the pH of alkali
solutions, and so in liming will tend to lower the pH and thus
reduce the chance of damage being done to the skin.

The use of a saturated solution of slaked lime in the liming
process enables a very considerable swelling of the hide to take
place but fixes the maximum pH attainable at pH 12·5. The
swollen condition facilitates the enzyme action in the bating
process in removing the elastin, and the organic acids so formed
cause the pH to fall to about 7·5. This results in the " falling "
of the skin, but care must be taken to see that the pH does not
become so low as 5·5-6·0, which happens to be the range in which
the putrefactive bacteria become active. Before any of the usual
tanning processes can be applied the pH has to be brought still
lower, and it is this which requires careful control for much of the
success or failure of tanning will depend upon it. This is effected
by either " drenching " or " pickling ." For vegetable tanning the
liquors are usually below pH 5, and for chrome tanning below
pH 4. It is necessary, therefore, to bring the pH below that of
the isoelectric point of collagen, pH 4·7.

CHAPTER XXI.

CHROME TANNING AND OTHER MINERAL TANNING PROCESSES.

The Importance of Hydrogen-Ion Concentration.

OF the several mineral tannages which have been proposed, only those involving the use of basic chromium salt solutions have as yet been adopted to any great extent. Basic alum solutions are sometimes employed for certain types of leathers, and owing to the exigencies of the war Germany was compelled to use iron tannages. Chrome-tanned leathers have many good points which tend to make them superior to vegetable-tanned leathers. In chrome-tanned leather the amount of tanning material is about 5 per cent. of the finished leather as compared with 50 per cent. in the vegetable-tanned leather, and consequently the larger amount of filling, usually grease and wax, required by the former confers on it desirable preserving qualities. On account of their water-proofness and durability, chrome leathers are used in the uppers of the better quality boots, in soles, harness, belting and hydraulic leathers. Other mineral tannages have been tried, *e.g.*, titanium salts, tin salts, silicates, and in some cases they have been patented, but it is probable that hitherto the extent of their practical application is small. It happens then that the metal salts which have passed into general use in the tannery are those of chromium, aluminium, and ferric iron.

The fact that salts of those metallic bases, which as far as their precipitation pH's are concerned (*vide* Britton, *J. Chem. Soc.*, 1925, **127**, 2157), appear to be among the weakest is significant, and so also is the fact that the salt solutions of these particular bases can be rendered appreciably basic by the addition of alkalis or hydrolysing agents before a precipitate begins to appear. This extremely important power of forming " *soluble basic salts* " has a profound influence upon the reactions of chromium salts (*J. Chem. Soc.*, 1925, **127**, 2120 ; 1926, **125**, 270). Their importance in chrome tanning and the reverse process of extracting (stripping) chromium oxide from leather, thereby rendering leather scrap

available for glue manufacture, will be discussed in this chapter and also in Chapter XXII. which will deal more particularly with chrome liquors and the theory of chrome tanning.

Chrome Tanning.

It was pointed out in the previous chapter that it was advisable to bring the pH of the skin or pelt somewhere near to that of the isoelectric point of collagen. At this point the pelt is more penetrable to tanning liquors than it is when swollen on either the acid or alkaline side of the isoelectric point. To have the pelt in the maximum " fallen " condition is also an advantage as far as chrome tanning is concerned, for this will tend to lessen the " emptiness " of the chrome tannage. There is much controversy regarding the state of the chrome-tanning liquors as to whether they should be nearly on the point of precipitation, and whether regulation of their hydrogen-ion concentrations is really necessary. There is, however, no doubt that both these factors do play important parts. Much depends upon the pH of the pelt immediately before tanning, and the extent by which it may be removed from that isoelectric point through the acidity of the tanning liquors. The nature of the chrome-tanning bath and the reactions in which the hide substance participates very probably causes hydrogen-ion concentrations to be set up within the skin which are very different from those ruling in the baths. It is generally agreed that pelt tanned whilst in the " fallen " state tends to be soft and pliable, whereas in the swollen state it is often hard and brittle. The swelling which takes place in the chrome bath somewhat impedes tanning, but the rate of tanning is of secondary importance when the quality of leather required is considered. The hydrogen-ion concentration of the tanning liquor is certainly one of the main factors which determine the properties of the resulting leather.

We shall now consider the various types of liquors used in chrome tanning. They fall in either one of two categories : (1) one-bath processes, and (2) two-bath processes. Both classes are in effect the same : in the one-bath processes the pelt is immersed in a soluble basic chromium salt solution, usually the sulphate ; and in the two-bath process the pelt is first immersed in a chromic acid solution or an acidified solution of potassium or sodium dichromate, then removed and allowed to stand for some time in the dark, and finally immersed in solution containing an excess of sodium thiosulphate and carefully regulated amounts of hydrochloric acid. The first practical method was introduced

by Knapp in 1858, and comprised basic chromium chloride, made so by the addition of sodium hydroxide. This process was resuscitated in 1893 by Martin Dennis, who patented chromium chloride to which sodium carbonate had been added in an amount insufficient to produce precipitation. Eitner in 1881 employed basic chromium sulphate solution of approximately the composition $CrOHSO_4$, prepared by adding caustic soda to chrome alum. Balderston (*J. Amer. Leather Chemists' Assoc.*, 1924, **19**, 105) prepared the same bath by reducing sodium dichromate with a current of sulphur dioxide, thus : $Na_2Cr_2O_7 + 3SO_2 + H_2O \rightarrow 2Cr(OH)SO_4 + Na_2SO_4$. The excess of sulphur dioxide, in giving increased acidity, will have some effect upon the tannage. Other methods of preparing the one-bath tanning liquors from dichromates are employed. A method due to Procter (*Leather Trades Review*, January 12, 1897) brings about the reduction with sugar or other carbohydrates in presence of such a limited quantity of hydrochloric acid as to produce a basic salt. Thus, a solution may be made by dissolving 3 parts of sodium or potassium dichromate in a convenient amount of water, adding 6 parts by weight of concentrated hydrochloric acid, and then cane sugar or glucose carefully until a green solution is obtained which may be made up to 100 parts. Such a solution has about the same concentration as that of a 10 per cent. solution of basic chrome alum. Eberle has patented " Chromalin " (D.R.P. 119042/1898, 130678/1899), which is a dichromate reduced with organic substances, *e.g.*, glycerine, glucose sugar, starch. Burton and Glover (B.P. 184360/1921) reduce with tea-dust in hydrochloric or sulphuric acid solutions. Heinzerling (1879) used a solution of potassium dichromate and ordinary alum. The chromic acid fixed suffered reduction by the organic material of the skin. This method was not a commercial success ; it was, in effect, a combined chrome-alumina tannage. Another unsuccessful combined tannage, that of iron and chrome, was advanced by Cavallin, in which the pelt was first impregnated with potassium dichromate solution and reduction subsequently effected by treatment with a solution of ferrous sulphate. This is an example of a two-bath tannage. The first chrome-tanning process to meet with commercial success was that due to Schultz, in which the first bath was acidified potassium dichromate and the second acidified sodium thiosulphate. Despite the simplicity, ease of control, and efficiency of the one-bath scheme, the Schultz method still finds wide application for the manufacture of both light and heavy leathers. Many modifications of the two kinds of tanning have been patented, the single baths usually containing certain sodium

salts—*e.g.*, acetates, formates, etc.—and the double baths differing in the reducing agent employed, *e.g.*, sulphites of sodium and sulphurous acid solutions of alumina and zinc oxide (*cf.* Hirsch, U.S.P. 1404957/1922).

One-Bath Chrome Tanning.

Some experiments by Lumière and Seyewetz (*Bull. Soc. Chim.*, 1903 (3), **29**, 1077) on the action of chromic salt solutions on sheets of gelatin and gelatin sols throw some light on the chrome-tanning action. Chrome alum and most of the normal chromic salts when added in adequate amounts render the gelatin insoluble, even in boiling water, and imputrescible. The ratio of chromium to acid radical in the solution before and after treatment was nearly the same, indicating that the chromic salt must have been taken up as such by the gelatin. By repeated washing with boiling water of the gelatin tanned with chromic sulphate, much of the acid radical was removed ; the gelatin swelled and some passed into solution. When, however, the gelatin was treated with dilute alkali it was found possible to extract the acid without either causing it to swell or to become soluble. It had previously been found by Namias that the power of chrome alum solution to tan gelatin was increased if alkali were added to it until precipitation was about to begin. Lumière and Seyewetz found that Recoura's green basic sulphate ($2Cr_2O_3,5SO_3$) caused the gelatin to resist repeated washing much more satisfactorily. Procter and Law (*Collegium*, 1909, **326**, 199, 209) studied the diffusion of basic chromium, ferric and aluminium salt solutions into gelatin jellies and found, by observing the movement of a red phenol-phthalein boundary, that the acid always diffused into the jellies more quickly, continually making the salt more and more basic until a part became incapable of further diffusion and then precipitated within the jellies. In time the mother-liquors became more acid, but the precipitates formed in the jellies could be re-dissolved only by means of considerably acid solutions. Stiasny (*Collegium*, 1908, **325**, 337) obtained quantitative evidence of the fact that the ratio of acid radical to chromium in the tanning solution became smaller as the pelt underwent tanning. He experimented upon cubes of butt in chromium sulphate solution and in a basic chromium sulphate solution. Table 90 gives some of his results, the ratio of acid radical being recorded as parts by weight of SO_4 combined with 52 parts of chromium (*i.e.*, At. Wt.).

It will be observed that in both cases a very rapid absorption by the pelt of sulphate occurred, such that the ratios of parts of

TABLE 90.

SHOWING VARIATION IN CR : SO$_4$ IN TANNING LIQUOR AND IN BASIC SULPHATE FIXED BY PELT.

(a) *Chromium Sulphate.*

Time after beginning of Tanning.	Original.	15 min.	1 hour.	4 hours.	24 hours.	48 hours.
Parts SO$_4$ in Liquor	146·1	133·3	123·3	118·2	121·7	130·3
Parts SO$_4$ in Pelt .	—	792	449	257	93·4	—

(b) *Basic Chromium Sulphate* [Cr (OH)$_{0·9}$ (SO$_4$)$_{1·1}$].

Parts SO$_4$ in Liquor	105·5	100·4	101·2	—	102·1	102·9
Parts SO$_4$ in Pelt .	—	208	92·4	—	89·4	—

Cr : parts SO$_4$ therein were considerably higher than that, *viz.*, 144 parts SO$_4$, required to form the normal chromium sulphate. The pelt immersed in the normal sulphate solution contained, however, 93·4 parts SO$_4$ after 24 hours (*i.e.*, ≡ Cr$_2$O$_3$,1·94SO$_4$), whereas the other contained 92·4 (≡ Cr$_2$O$_3$,1·92SO$_4$) within an hour. The sulphate ratio in the normal sulphate solution shows that it first became basic, but as the chromium salt absorbed by the pelt became basic, so also did the solution become less basic. More extensive investigations have been made by Thomas and Kelly (*J. Amer. Leather Trades, C.A.*, 1920, **15**, 487) and Thomas, Baldwin and Kelly (*ibid.*, p. 147) on hide powder over longer periods. They followed the composition of the tanning liquor and the powder from time to time and also recorded the variations in hydrogen-ion concentration of the solutions. The former workers used 5 gms. of hide powder in 200 c.c. of ordinary chromium sulphate solution containing 16·4 gms. of chromium oxide per litre, and the latter, using the same quantities, employed as their tanning liquor a stock chrome liquor (Cr$_2$O$_3$ 215·0 gms. per litre, SO$_3$ 219·0 ; Fe$_2$O$_3$ 30·9 ; Al$_2$O$_3$ 3·2 ; and NaCl 6·5) diluted to 16·98 gms. Cr$_2$O$_3$ per litre. If the amount of sulphate in combination with the iron oxide and the alumina be neglected, it is found that the composition of the basic chromium sulphate in the solution corresponded with Cr(OH)$_{1·06}$(SO$_4$)$_{0·97}$. The tanning solutions are thus approximately the same with respect to their chromium content and the two series of experiments become comparable. The data given in Table 91 were compiled from their results.

This table shows that from tanning solutions of equal chromium content (*a*) there was an initial increase in *p*H, but one which was

TABLE 91.

Tanning Liquor.	$Cr_2(SO_4)_3$.			$Cr(OH)_{1\cdot06}(SO_4)_{0\cdot97}$.		
	pH of Liquor.	Composition of Hide Powder.		pH of Liquor.	Composition of Hide Powder.	
Time.		$\%$ Cr_2O_3.	Mols. SO_3 $1Cr_2O_3$.		$\%$ Cr_2O_3.	Mols. SO_3 $1Cr_2O_3$.
1 hour .	2·12	1·5	4·0	3·19	3·5	3·6
2 hours .	2·09	2·2	3·2	3·14	5·6	2·1
4 ,, .	2·03	3·8	3·4	3·16	6·9	1·9
6 ,, .	2·00	4·5	2·1	3·19	7·7	1·9
8 ,, .	1·97	5·3	2·0	3·20	8·0	1·8
12 ,, .	1·91	6·3	1·9	3·22	8·6	1·9
1 day .	1·95	7·7	1·8	3·26	—	1·7
2 days .	2·04	8·5	1·8	3·28	10·4	1·7
3 ,, .	2·08	8·9	1·8	3·25	10·8	1·7
4 ,, .	2·10	9·2	1·8	3·21	11·0	1·7
8 ,, .	—	9·9	1·8	—	—	—
16 ,, .	2·08	10·1	1·9	—	—	—
32 ,, .	2·11	10·7	1·8	—	—	—
64 ,, .	—	10·7	1·8	—	—	—

much greater in the ordinary sulphate solution, followed by a gradual increase in pH, (b) the chromium absorption, and therefore tanning action, was more rapid from the basic solution, (c) the ultimate composition and amounts of the basic chromium sulphate taken up by the hide powder from the two solutions were approximately the same. The amount of chromium oxide absorbed from the basic sulphate solutions in 48 hours shows that in that time the tanning effected was nearly at a maximum, for very little absorption took place subsequently.

Hitherto nothing has been said of the effects which may be produced by varying the concentration of tanning liquors, and also the " basic-ness " of the liquors. These are shown by the curves given in Fig. 82, which illustrate the results obtained by Thomas and Kelly (*Ind. Eng. Chem.*, 1921, **13**, 65), Baldwin (*J. Amer. Leather T.C.A.*, 1919, **14**, 433), and Gustavson and Widen (*Ind. Eng. Chem.*, 1925, **17**, 577) with hide powder. The curves representing Baldwin's and Thomas and Kelly's data are denoted by their names, the others refer to Gustavson and Widen's work. The compositions of the basic solutes are given in the diagram and also the various pH ranges of the different liquors. The chrome solutions used by Baldwin, Thomas, and Kelly were apparently impure commercial liquors and their results, therefore, are not strictly comparable with those of Gustavson and Widen, who took special precautions to prepare pure solutions. Gustavson and Widen record

only one series of sulphate contents of their tanned hide substance, obtained from the solutions of 53·5 per cent. " basicity " (*vide infra*), *i.e.*, those corresponding to $Cr(OH)_{1·61}(SO_4)_{0·70}$. The chromium sulphate fixed agreed on the average with $Cr_2O_3,1·64SO_3$; the variations from these molar proportions being small. Thomas and Kelly's data reveal that the basic chromium sulphate in the powders contained between 1·5 to 1·7 mols. SO_3 to $1Cr_2O_3$ tanned by those liquors containing up to 73 gms. Cr_2O_3 per litre. Thereafter, the sulphate content increased, and in one case exceeded 3 mols. Baldwin's data indicate more than 2 mols. SO_3 to $1Cr_2O_3$ in the hide substance immersed in the dilute solutions of less than
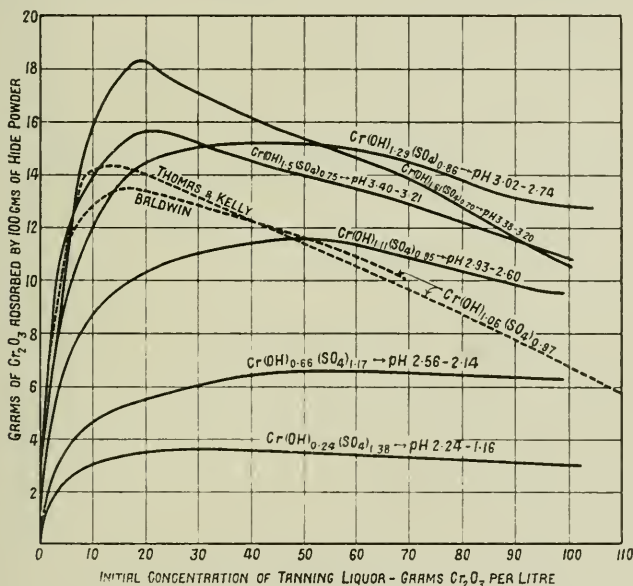
FIG. 82.—Absorption of Basic Chromium Sulphate by Hide Powder.

2 gms. Cr_2O_3 per litre; and from 2-25 gms. Cr_2O_3 per litre solutions it remained fairly constant at 1·8 mols., and then increased to 2·5 mols. in the substance with 66·4 gms. chrome per litre solution.

The absorption curves in Fig. 82 show that there are two factors which have considerable influence on the amount of basic chromium sulphate, fixed by hide powder, *viz.*, (1) the degree of " basic-ness " of the chrome liquor, and (2) the concentration of the liquor. The optimum fixation was produced by those solutions which had been rendered basic to the maximum extent. According to the curves of Baldwin, Thomas, and Kelly, it would

seem that the most efficient concentrations lay between 10 and 20 gms. chromic oxide per litre. From Gustavson and Widen's curves it is seen that from the two most basic solutions—$Cr(OH)_{1\cdot6}(SO_4)_{0\cdot7}$ and $Cr(OH)_{1\cdot5}(SO_4)_{0\cdot75}$—the greatest absorption occurred when the liquors contained about 20 gms Cr_2O_3 per litre. Whilst the absorptions which took place from the less basic solutions of this chromic oxide concentration had not attained their respective maxima, the increased fixations which accompanied further increases in concentration of the various chrome liquors were not considerable. The curves also show the superiority of chrome liquors in which the chromium sulphate corresponded with $Cr(OH)SO_4$, or were even more basic. It is interesting to note that the pH of the liquors increased as their " basicity " increased, varying from pH 1·16 for the most concentrated solutions of the least basic salts, to pH 3·38 for the least concentrated of the most basic solutions. The hydrogen-ion concentration of those solutions which produced most efficient tanning was in the region of pH 3. *They were not, however, buffered at this value, and on the withdrawal of any acid such as would occur in reacting with collagen, the pH would undergo a sudden increase, and in consequence precipitation within the pelt would eventually ensue.* This, it is believed, is what happens to that liquor which finds its way into the pelt, the fibres of which thereby become tanned. If this be the case, then the pH inside the pelt will be much higher, with its resultant effect on its swelling, than in the external liquor. Hence it is evident that the process of tanning will be largely facilitated by maintaining as high a pH in the external liquor as possible.

The problem of finding some suitable method of expressing the degree of " basic-ness "—technically, though erroneously, termed " basicity "—of chrome liquors has been one of some difficulty. Of the several methods which are used, two have gained general use : (1) to give the number of parts by weight of SO_4 combined with 52 parts of Cr ; thus 144 parts correspond with $Cr_2(SO_4)_3$, 96 parts $CrOHSO_4$, 48 parts $Cr(OH)_2(SO_4)_{0\cdot5}$; (2) to express it as the percentage weight of chromium in combination with basic groups (OH) of the total weight of chromium in combination with both hydroxyl and acid groups, *e.g.*, 33·3 per cent. basicity corresponds to $Cr(OH)SO_4$; 66·7 per cent. to $Cr(OH)_2(SO_4)_{0\cdot5}$ and 0 per cent. with $Cr_2(SO_4)_3$. Though the first method has been widely used in this country and on the Continent, it is rapidly being superseded by the second method.

In order to vary the basicity and hence the stability of chrome tanning liquors so as to obtain some desired quality in the resulting leather, certain acids and salts are sometimes included in the baths.

Neutral salts, *e.g.*, the chlorides and sulphates of the alkali metals, bring about a suppression of the swelling of the pelt, and, according to the experiments of Burton and Glover (*J.I. Soc. Leather T.C.*, 1922, **6**, 6), with basic chromium sulphate solutions on calf skin, ox-hide and cow-hide, they retard the penetration of chromium into the pelt. This retardation was greater with both sodium and potassium sulphates than with sodium chloride, though it should be mentioned that the amounts of sulphate fixed by the pelt in presence of sodium chloride were initially greater, but tended to become equal after very protracted periods of immersion (about 90 days). Their results concerning the influence which the basicity of the chrome liquor has on the rate of tanning, *viz.*, the greater the basicity the greater the speed at which chrome absorption proceeds, are in accord with those given by hide powder. Burton and Glover (*ibid.*, 1921, **5**, 183) obtained analogous results with gelatin. Other substances are sometimes put into, or are developed in, the chrome baths, *e.g.*, acetates, formates, hydroxy-compounds, oxalates, sulphites, in order to modify their tanning action either by bringing the pH of the liquors nearer to the isoelectric pH, or by making precipitation of basic chrome salts more difficult. The effects thus obtained will be discussed in the next chapter.

Neutralisation of Chrome-Tanned Leather.

It will be inferred from Tables 90 and 91 that the chrome substance fixed by leather has the molecular proportions of an indefinite basic salt. Some of the acid radical on coming into contact with water becomes hydrolysable, and in order that the leather shall not deteriorate, and that fatty acids shall not be precipitated and so produce unsatisfactory surfaces when the leather is subjected to the " fat-liquoring " process, it is essential to neutralise to about pH 6 after tanning. Fat-liquoring should be carried out immediately afterwards so that the acid in the inside of the leather will not have had time to reach the surface. This, however, will be neutralised as soon as the fat-liquor penetrates through the leather. Over-neutralisation will decompose the basic chrome salt, and besides impairing the appearance of the leather, will reduce its tensile strength to give a hard " tinny " leather. The decomposition of the fat-liquor through under-neutralisation will impart to the leather a rough surface, and there will be a pronounced tendency for the leather to crack on drying (Procter and Griffith, *J.A.L.C.A.*, 1917, 612 ; Burton, *J.I.S.L.T.C.* 1922, **6**, 160). Stiasny's mixture (*Collegium*, 1912, **11**, 293) is regarded as a perfectly safe neutralising agent, in that it cannot lead

to over-neutralisation. It comprises a 2 per cent. Na_2CO_3 solution containing 2 per cent., or more if necessary, of ammonium chloride or sulphate. In this case the liberated carbon dioxide and the ammonium salt both exert a buffering action to prevent the pH from rising too high. Sodium bicarbonate and borax are among the safest neutralising agents, though should they be added in excess, the grain dries to a horny surface. Eitner advocated sodium silicate, but this has the disadvantage if used in excess of causing the deposition of too much colloidal silica on the hide fibres, thus producing a brittle leather. With sodium thiosulphate, even when added in excess, there can be no possibility of over-neutralising, and this is also true with sodium phosphate, Na_2HPO_4, for both automatically regulate the pH to a suitable value. The former sets sulphur free which affects the colour of the leather, and the latter replaces some of the sulphate (or chloride) in the leather by phosphate to produce a fuller leather. Chrome sole leathers are not usually fat-liquored, and sometimes not even neutralised, but are dried out and impregnated with a mixture of melted waxes and rosin, which give firmness and water-resistance.

Other Mineral Tannages.

Tanning, or " tawing," with alum and sodium chloride solutions, the latter being used to reduce swelling, and the alum very often made basic, is resorted to in the manufacture of glove leather, and also for the preservation of the skins of fur and hair rugs. After the skins have been rubbed with a mixture of egg-yolk, cotton-seed oil, and flour, they are aged for considerable periods, when the precipitated basic aluminium sulphate becomes difficultly soluble, and so tends to become fixed. Then the excess of salt is removed by soaking, and the leather finished as desired.

Iron-tanning, by means of basic ferric salts, though it has had some considerable application, cannot be considered satisfactory. The basic ferric salt deposited in the leather in time becomes reduced to the ferrous state by the leather itself, which as a consequence undergoes slow oxidation and so deteriorates. Another disadvantage is the extreme difficulty to neutralise the leather, for on neutralisation the iron salt becomes colloidally dispersed and is washed out of the leather (Jettmar, *Cuir*, 1919, **8**, 106). Iron-tanned leathers are decomposed, and become tender, by water (Moeller, *Z. Leder u. Gerberei Chem.*, 1922, **1**, 166).

M. C. Lamb (F.P. 327945/1902) patented the use of basic solutions of titanic salts, *e.g.*, the basic sulphate, chloride, and oxalate, and pointed out that both tanning and dyeing, the deposited

titanium basic salt acting as a mordant, could be effected simultaneously.

Hough (*Cuir*, 1919, 209, 257, and 314) has shown that good leathers can be obtained by tanning with silica by immersing in a 30 per cent. solution of hydrochloric acid, into which a 30 per cent. solution of sodium silicate is poured until the free acid is decinormal. Swelling is kept down by adding salt to the bath. Adding the reactants in the opposite manner leads to unsatisfactory tanning.

Other salts which are stated to have tanning action are those of the rare earths, tin, zinc, thorium, zirconium, and beryllium (Parenzo, *Collegium*, 1910, 121 ; Zacharias, *C.B.*, 1903, **2,** 536 ; Jettmar, *Chromgerbung*, Leipzig, 1924, 28). Salt solutions of many of these metals can be rendered appreciably basic before the respective hydroxides begin to precipitate.

CHAPTER XXII.

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATIONS OF CHROME TANNING LIQUORS.

To a great extent the quality of chrome leathers is a question of the chrome liquors used in the manufacture. This chapter deals with the modes by which the tanning properties of chrome solutions may be varied. It should be mentioned that the salts of tervalent chromium exhibit in a unique way the phenomenon of " soluble basic salt " formation, on which the process of tanning very largely depends. In connexion with some researches on the pH's at which various hydroxides becomes precipitable (*J. Chem. Soc.*, 1925, **127**, 2127) the author observed that from a very dilute solution of ordinary chrome alum (*i.e.*, violet) precipitation did not begin until 1·0 equivalent of NaOH had been added for each atom of Cr present when a pH 5·3 had been attained, and for precipitation from an ordinary chromium chloride solution 1·07 equivalent of alkali was necessary, the pH then being 5·28. It would seem that soluble basic salts were formed having approximately the formula $Cr(OH)R_2$, where R = Cl or $\frac{1}{2}SO_4$ (see p. 264).

Fig. 83 gives the precipitation curve of violet chrome alum, starting at a pH of 3·2, which indicates that the combined sulphuric acid had become hydrolysed to the extent of 2·2 per cent., and showing a rapid pH increase during the addition of the first equivalent of alkali. The figures on the various curves denote the number of equivalents of alkali. The ordinary chromium chloride curve is exactly similar. If, however, chromium salts are boiled, cooled, and treated with alkali it will be found that more alkali has to be added before precipitation can ensue. The solutions also change in colour, becoming green, when considerable amounts of acid become hydrolysed. Thus, in the author's experiments 5 min. boiling produced in a chromium chloride solution an increase in hydrolysis from 1·6 to 16·2 per cent., and in the case of chrome alum from 2·2 to 28·7 per cent. The precipitability in the cold of the chloride as silver chloride from green chromium chloride solutions, and of the sulphate as barium sulphate from chromium sulphate and chrome alum solutions is

far from complete. The proportion of chloride precipitated depends upon the silver salt used, whether it contains the radical of weak acid or of a strong acid, the acid present and the temperature. The curve for green chrome alum is given in Fig. 83, from which it will be seen that the change in pH, compared with the almost rectilinear change produced by the violet chrome alum solution, undergone prior to precipitation is similar to that of neutralisation of an acid. Precipitation began with 1·2 equiva-
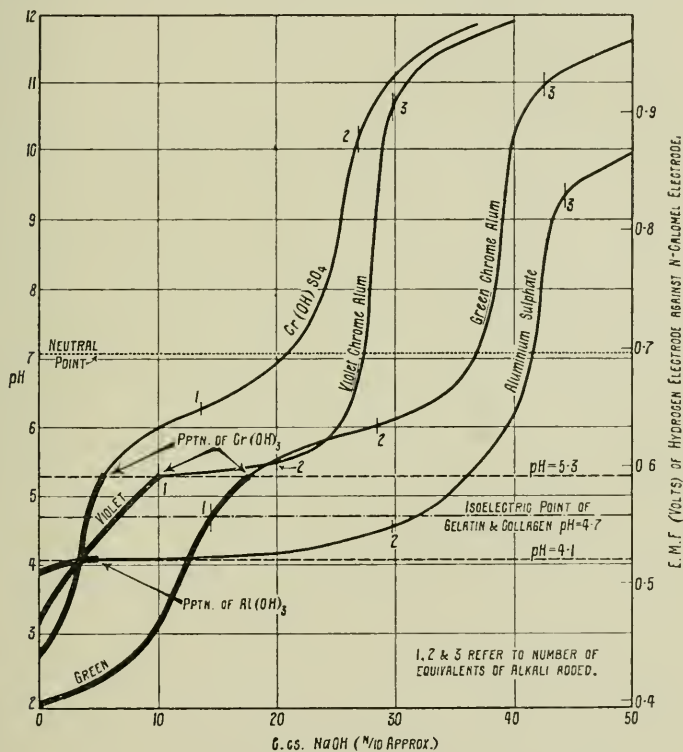
FIG. 83.—Precipitation Curve of Violet Chrome Alum.

lents, whereas it did not occur from the green chloride solution until 1·4 equivalents of alkali had been added.

It is interesting to recall that the tanning powers of the green solutions are less than those of the corresponding violet or blue solutions, due evidently to the greatly increased acidities, *i.e.*, lower pH's. Thus, Burton (*J.I.S. Leather T.C.*, 1918, 2, 205) points out that violet chrome alum solutions tan more rapidly than do the green solutions. The exponents of Werner's

co-ordinate theory try to account for the change from the violet salt to the green state by a change in molecular orientation, *e.g.*, $[Cr(H_2O)_6]Cl_3 \rightleftharpoons [Cr(H_2O)_4Cl_2]Cl,2H_2O$ but in the opinion of the author it appears that no satisfactory and unequivocal evidence has yet been brought forward to support such a contention. There is very strong evidence that the green solutions correspond to the border line condition between that of true solution and colloidal solution, and they are perhaps best regarded as a form of colloidal electrolyte. This view is incidentally one which helps to provide an explanation of chrome tanning.

As the Werner Theory has been accepted by such well-known leather chemists as Stiasny and Gustavson, it is perhaps desirable to point out here some of the evidence on which Werner based its application to chromium chloride solutions, especially as hydrogen-ion concentration measurements tend to lead to another explanation.

Werner and Gubser (*Ber.*, 1901, **34**, 1579) first applied the theory to chromium chloride, and quite recently Lamb and Fonda (*J. Amer. Chem. Soc.*, 1921, **43**, 1154) referred to its application to chromium salts as " perhaps the most striking exemplification of the Werner theory of molecular structure." It is therefore surprising that the evidence on which Werner and Gubser based their views are quite unconvincing, and indeed, the difference might well be due to the existence in the green solutions of basic aggregates which are essentially colloidal in nature. The low conductivity of solutions of the green form of chromium chloride was regarded as evidence of the dissociation of a binary salt, $(CrCl_2,4H_2O)Cl,2H_2O$. The abnormal molecular weights calculated from the depression of the freezing-point were supposed to supply fundamental evidence for this structure of the green form, for they happened to be of the order of one-half the molecular weight of hexahydrated chromium chloride. It is strange that the weight of six molecules of water should have been included in the latter molecular weight, seeing that four molecules only are supposed to be present in the nucleus of the complex chromium kation. The observed molecular weights of the violet chromium chloride were of the order of one-quarter of that of the hexahydrated salt, and this was taken as being due to $(Cr6H_2O)Cl_3$. The results show, however, that the observed molecular weights of the violet chloride in the more dilute solutions are somewhat too high—this may be regarded as due to incomplete ionisation—but it is surprising to find that the agreement between the observed and the theoretical values only becomes perfect for a 12 per cent. solution, in which the dissociation must be far from

complete. Werner and Gubser tried to confirm the view that only one chlorine atom in the green form was ionisable and there-fore precipitable with silver nitrate, but they always found that the amounts precipitated were greater than corresponded to one atom, even in rapid estimations carried out at o°. Similar observations have also been made on the incomplete precipitation with barium chloride from green chromium sulphate solutions. It is difficult to reconcile with the co-ordination theory the observations of Weinland and Koch (Z. anorg. Chem., 1904, **39**, 296) on the pre-cipitability of chlorine from green chromium chloride solutions with various silver salts, both in presence and in absence of free acid. The amount of chlorine precipitated depended on the nature and the quantity of the particular silver salt used ; without the addition of acids, all the silver salts precipitated at least two-thirds of the chloride. The presence of nitric acid had the effect of diminishing the amount of chloride liberated, whereas the silver salts of weak acids, such as acetic, lactic, and nitrous, and silver sulphate im-mediately precipitated all the chloride. Silver salts of strong acids did not cause complete precipitation and free strong acids sup-pressed the precipitation even more. Lamb (J. Amer. Chem. Soc., 1906, **28**, 1710 ; Lamb and Fonda, ibid., 1921, **43,** 1154) tried to explain the above observations by a gradual transition from the green variety to the violet due to the hydrogen-ion concentrations ruling during the reactions, but in order to show how the transformation took place they found it necessary to postulate further that the green variety first underwent hydrolysis to form some such basic complex as $CrCl_2OH$.

Precipitation from both the violet and green forms is dependent on the attainment of a hydrion concentration of about pH 5·3. It begins from those solutions which contain chromium in the normal condition when about one equivalent of sodium hydroxide has been added, whilst the green solutions do not yield precipitates until somewhat larger proportions of alkali have been added. The greater amounts of alkali required in the latter case show that the change produced in the solutions on turning from violet or blue to green has rendered the chromium salts more resistant in their behaviour towards alkali.

It is probable that the basic chromium complexes which seem to be present in green solutions are " micellar " in structure and constitute a colloidal electrolyte in which the kations are composed of chromium hydroxide and varying amounts of acid radical, a portion only being ionisable. This would account for the slow-ness with which silver chloride and barium sulphate may be pre-cipitated from the appropriate green solutions, and this is especially

so when the chromium solutions happen to be basic, such as may be prepared from the basic glassy masses obtained by evaporating solutions of chromium salts to dryness. There appears to be a tendency for one-third of the combined acid in a chromium salt, i.e., the amount corresponding to that which seems to be loosely combined and gives rise to the formation of the " soluble basic salt," to be driven off on evaporation. Thus a basic salt prepared in this way had a composition corresponding to $Cr(OH)SO_4$ and gave in solution no precipitate with barium chloride ; neither did it do so with ammonia except on boiling or keeping. The soluble basic complexes in the green solutions have some properties in common with chromium hydroxide. Chromium hydroxide which has been suspended in water and boiled, or has been allowed to stand, becomes difficultly soluble in acids, as is also the case with ferric hydroxide, slowly dissolving only in concentrated acid solutions. Hence it is evident why the acids present in Weinland and Koch's experiments did not immediately decompose the green salt and render the chloride available for precipitation, and why the acid actually retarded the precipitation by depressing the ionisation of the colloidal electrolyte. The conception of basic aggregates also supplies an explanation why it was only the silver salts of weak acids which caused nearly all the silver chloride to be precipitated. The first reaction taking place between the precipitant and the colloidal electrolyte is one of double decomposition, whereby the chloride anion of the chromium complex is replaced by the anion of a weak acid. This would diminish the hydrogen-ion concentration of the solution, which would therefore tend to approach the value requisite for the precipitation of chromium hydroxide ; the basic complexes would thus be rendered so unstable that the chloride radicals in them would become susceptible to reaction with the silver salt.

Other properties which accompany the change in colour from violet to green in chromium salts solutions are : (1) increase in conductivity without any comparable change in cryoscopic measurements ; (2) increase in volume of the solutions ; (3) on dialysing green sulphate solutions the liquid in the dialyser becomes increasingly basic whereas the violet salts pass through as such ; (4) green salts are much more occluded by precipitates ; (5) absorption spectra of green solutions are similar to that produced by colloidal chromium hydroxide ; (6) migration experiments of green solutions are unconvincing as far as any possible complex formation is concerned. It appears highly probable that green chromium salt solutions contain some chromium hydroxide in the colloidal condition, which view seems to be supported by the

viscosity data of Partington and Tweedy (*Nature*, March 20, 1926) of solutions of the violet and green chromium chloride. They found that the viscosities of the violet solutions were higher than those of the corresponding green solutions. Thus it would be expected that the viscosities of green solutions would be lower than those of violet solutions of the same concentration, for the appreciable amounts of hydrochloric acid hydrolysed will give rise to diminished viscosities, and, as is well known, the viscosity of metallic oxide hydrosols is usually very little higher than that of water, which very probably is also true of hydrosols of basic chromium chloride (*vide* Yeo and Freyer, *Jour. Phys. Chem.*, 1926, **30**, 1389—these workers also found that the viscosity of basic chromium chloride hydrosols was affected by their pH). The curve in Fig. 83, marked $Cr(OH)SO_4$, corresponds to a solution prepared by reducing a solution (100 c.c.) of potassium dichromate with sulphur dioxide and boiling until any excess of gas had been expelled. The pH 2·7 of this solution compares with those of basic chrome liquors, and is remarkably lower than that attained, pH 5·3, when the violet chrome alum had attained such a basicity and was on the point of precipitation. Barium chloride gave a partial precipitation from this solution, suggesting that some sulphate had become locked up by the colloidal aggregates. This solution did not yield a precipitate with alkali until pH 5·3 was reached. The solution then corresponded with $Cr(OH)_{1.4}$ $(SO_4)_{0.8}$. *It is an interesting fact that the two elements whose salts should have gained importance as tanning agents are chromium and aluminium, for it happens that the precipitation pH's of their hydroxides are very close to that of the isoelectric point of collagen, pH 4·8 ; pH of $Cr(OH)_3$ 5·3 ; pH of $Al(OH)_3$ 4·2.* Ferric salts on being rendered basic become colloidal in strongly acid solutions, and coagulate in the region of true neutrality (Britton, *J. Chem. Soc.*, 1925, **127**, 2152). Titanic salts which have been patented as tanning agents by Lamb (French P. 327,945), and also used for leather mordanting purposes, on being made basic pass through a colloidal solution stage and precipitate, like ferric hydroxide, when almost the stoichiometrical amount of alkali has been added commencing at about pH 2·3 (F. J. Watson, private communication).

The ready hydrolysis which takes place even in strongly basic chromic sulphate solutions causes their pH's to be relatively low. Thus Thomas and Baldwin (*J. Amer. L.T.C.A.*, 1918, **13**, 192) found that a commercial tanning liquor corresponding to $Cr(OH)_{1.24}$ $(SO_4)_{0.88}$ and containing 231 grams Cr_2O_3 per litre had a pH of 2·31, but on dilution gave higher pH's, 3·0-3·6, for dilutions from

10 to 800, and these pH's became slightly higher after standing for a week, the basic sulphate having therefore become less hydrolysed. They examined the pH of basic sulphate solutions containing 13·86 grams Cr_2O_3 per litre, which had varying basicities after standing for 2 and for 50 days. They found that the more basic solutions, $Cr(OH)_{1·28}(SO_4)_{0·86}$ to $Cr(OH)_{1·6}(SO_4)_{0·7}$, hydrolysed, for they gave initially higher pH's, 3·35-4·27, fell after 2 days to pH 3·35-3·60 but underwent very little change in 50 days. The less basic solutions, $Cr(OH)_{1·28}(SO_4)_{0·86}$ to $Cr(OH)_{0·7}(SO_4)_{1·15}$, however, underwent the reverse change and increased in pH, from pH 3·2 — 1·7 to pH 3·3 — 2·5 after 2 days and to pH 3·3 — 2·9 after 50 days.

The introduction of the idea of *Precipitation Figures of Chrome Liquors* by McCandlish (*J.I.S. Leather T.C.*, 1917, 114) furnishes a useful means for characterising the tanning properties of a liquor. These figures are obtained by titrating 10 c.c. of clear liquor, after previous clarification with kaolin, with a $N/10$ or $N/20$-solution of an alkali. The precipitation point marks the limit to which chrome liquors can be rendered basic. Though solutions that are on the point of precipitation are not without tanning action, they cause an irregular deposition of the basic chromium salt in the pelt. Hence there will be a pronounced tendency for the coarse external layers of chrome to prevent the chrome liquors from penetrating into the interior of the pelt. It is found in practice that *the smaller the precipitation figure the greater will be the speed at which tanning will proceed*. Liquors, however, which have very small precipitation numbers very often lead to unsuccessful tanning, due to the rapid reaction of the free acid with the protein of the pelt and the resulting rapid separation of the basic chromium precipitate. The whole liquor may even become turbid. To avoid the possibility of the interior parts of the hide not becoming tanned, it is better to begin the tanning process by using a liquor from which the chrome does not precipitate to any great extent until after the liquor has had time to soak thoroughly into the skin. This may be accomplished by giving a preliminary tannage with a liquor having a high precipitation number, or, having regard to most suitable pH of the pelt during tanning, resource may be made to liquors from which precipitation has been retarded by the presence of such substances as oxalates, acetates, sulphites (*vide infra*, Stiasny). Burton, Wood, and Glover (*J.I.S. Leather T.C.*, 1923, **7**, 37) have studied the variation in precipitation figures and the pH's of violet and green chrome alum solutions (the latter produced by boiling) with increasing salt concentration. Table 92 has been calculated from their results :—

TABLE 92.

PRECIPITATION FIGURES.

Gms. of Chrome Alum per Litre.	Violet.			Green.		
	pH.	Pptn. fig. c.c. NaOH for complete pptn.	Equivs. OH to 1 Cr.	pH.	Pptn. fig. c.c. NaOH for complete pptn.	Equivs. OH to 1 Cr.
5	3·08	0·33	1·00	2·12	0·50	1·50
10	3·08	0·29	0·87	2·03	0·47	1·41
25	2·99	0·27	0·81	1·86	0·44	1·32
50	2·91	0·26	0·78	1·69	0·41	1·23
75	2·82	0·26	0·78	1·60	0·38	1·14
100	2·73	0·26	0·78	1·52	0·39	1·17

The difference in pH of the violet and green solutions compare well with those given in Fig. 83. The ratios given in the third and sixth columns become, when expressed as percentages, instead of fractions, the basicity numbers of the basic solutions that are on the point of precipitation. The table shows that, whereas the violet solutions may be rendered basic to the extent indicated by $Cr(OH)SO_4$ in dilute solutions, the extent diminishes to $Cr(OH)_{0.78}(SO_4)_{1.11}$ in the concentrated solutions. Green solutions varied from $Cr(OH)_{1.5}(SO_4)_{0.75}$ to $Cr(OH)_{1.17}(SO_4)_{0.91}$. These basic solutions compare with the types of solutions used for tanning. The precipitation figures of violet solutions slowly increase on ageing. When chrome liquors are prepared by reduction of chromic acid or dichromates, it is found that the reducing agent used and the mode in which the reduction is carried out has some effect on the precipitation figure, even though the basicities of the several solutions may be the same. Neutral salts present in the liquors may have great effect on the precipitation figures (*cf.* Wilson and Kern, *J.A.L.C.A.*, 1917, **12**, 445), their effect being, in general, to increase them. This is especially so with sodium chloride, very probably through the conversion of some basic sulphate into basic chloride, which in the case of the green variety causes precipitation to be delayed still further.

Sodium salts of organic acids have an exceptional influence upon chromium salt solutions. When first added they generally delay the precipitation with alkali, the extent of which depends on such factors as ageing or boiling of the solution, and they may even, if added in sufficient quantities, prevent precipitation altogether from taking place. This is true of acetates, oxalates, tartrates, citrates, and sulphites. In similar fashion, chromium

acetate and oxalate solutions may become on standing or after boiling not precipitable with alkali, and when precipitation does take place from solutions containing one of these salts in an inadequate amount, it is far from complete. It is not surprising, therefore, that both the solutions may in extreme circumstances be incapable of tanning, whereas in general their tanning action is considerably reduced.

The addition of sodium acetate to green chrome alum solution has been found by Burton (*J. Amer. L.C.A.*, 1923, **18**, 358) to raise the precipitation figure when first added, but after a short time if an adequate amount has been used to make it infinite, in other words, to prevent precipitation with alkali and hydrolysing agents. He concludes that sodium acetate does not improve tanning, but cites numerous recent patents protecting chrome liquors in which acetates are inserted. The
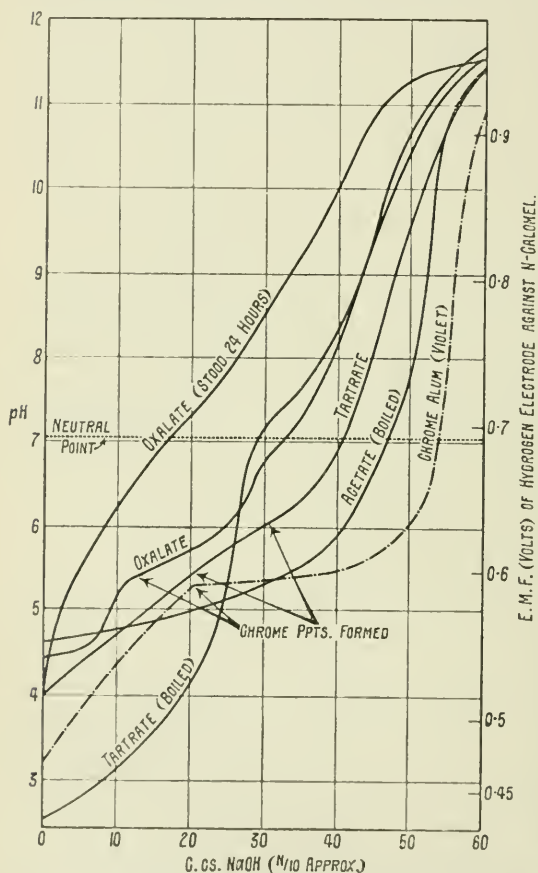
Fig. 84.—Addition of N/10 NaOH Solution to Chrome Alum Solutions containing Acetate Tartrate, etc.

author's studies (*J. Chem. Soc.*, 1926, 269) throw some light on the nature of the reactions which take place when these sodium salts are added to chromium salt solutions, and from the evidence obtained, he postulated the formation of somewhat stable but soluble basic aggregates, existing very probably in the form of colloidal electrolytes. Fig. 84 contains some *p*H curves which

show the variation in hydrogen-ion concentration produced when approximately decinormal sodium hydroxide was added at 18 C.° to chrome alum solutions to which either sodium acetate, or oxalate, or tartrate had been previously added.   They are of especial interest here in that they show how deeply seated may be the influence which these salts may have in either impeding or preventing precipitation from chromium salt solutions when reacted upon with alkalis.   They also explain why small quantities reduce the tanning power of the chrome liquors, whereas when added in larger amounts they render the liquors useless for tanning. It therefore becomes apparent why concentrated solutions of sodium acetate, oxalate, or tartrate are capable of dissolving chromium oxide, and why these solutions may be used as agents for stripping chromed leather, leaving the collagen for subsequent conversion into glue or gelatin.   The speed at which dissolution takes place is largely determined by the amount of ageing which the chromium oxide has undergone.   The curve corresponding to the titration of 100 c.c. M/100–chrome alum with N/10– NaOH is given in Fig. 84 for purposes of comparison.   The curve marked acetate is that of 100 c.c. M/100–chrome alum containing twice the stoichiometrical amount (*i.e.*, 12 mols. to 1 mol. of chrome alum) of sodium acetate, boiled for about 5 mins., cooled to 18° C. and 0·0900 N–NaOH added in presence of the hydrogen electrode. This solution was red, contained the chromium in a basic state, and gave no precipitate with alkali.   A similarly prepared solution but unboiled was precipitable.   The theoretical amount of alkali was 66·7 c.c.   The shape and position of the greater part of the curve is very similar to that of free acetic acid, as would be expected to be the case if the chromium were present in the solution in a basic state and much of the acetic acid had become hydrolysed (see *J.C.S.*, 1926, 275).   The two oxalate curves refer to the action of 0·1082 N–NaOH on 100 c.c. M/100–chrome alum to which 60 c.c. M/10–$Na_2C_2O_4$ had been added.   One had stood 24 hours at room temperature, in which time the solution became non-precipitable, whereas the other solution was titrated immediately and gave a precipitate with 12·5 c.c. of alkali (basicity of solution then being 22·5 per cent.) at *p*H 5·4.   (*N.B.*—*p*H $Cr(OH)_3$ is 5·3.)   The precipitation was partial.   The curves show surprisingly higher *p*H's than were given during a simple precipitation reaction. The same alkali was used in the tartrate titrations.   Both solutions contained 100 c.c. M/100–chrome alum and 30 c.c. M/10– sodium tartrate.   One was boiled for 5 mins. and thus rendered non-precipitable with alkali.   It was cooled to 18° C. and was ᵣed in colour but became green as the alkali was added.   The

unboiled solution gave a cloudiness with 20·2 c.c. of alkali (basicity = 36·4 per cent., pH 5·4), and the precipitate began to separate with 30·6 c.c. (basicity = 55·1 per cent., pH 6·5). Chromium tartrate solutions themselves are not precipitated with alkali ; neither are those chromium salt solutions to which sodium tartrate has been added in sufficient amounts. There is a risk that in chrome liquors made by reducing with organic matter (sugar, sawdust, etc.) organic acids may be formed, and these will have some effect on the tanning properties of the solution. Procter in his book on Leather Manufacture (1922, p. 265) called attention to the fact that *violet* solutions produced by the reducing with sugar should be avoided on account of their unsatisfactory tanning properties. The salts of these weak organic acids in basic chrome liquors would cause the liquors to assume pH's nearer to that of the isoelectric point of collagen, and in so doing would keep the swelling of the pelt at a minimum and thereby give rise to a softer and fuller leather. Procter and Wilson (*J. Soc. Chem. Ind.*, 1916, **35,** 156) found that solutions, if used in suitable concentrations of Rochelle salt (potassium sodium tartrate), sodium citrate, and sodium lactate, could be used to extract the chrome from tanned leather. H. G. Bennett (*Animal Proteins*, p. 135) has also shown that the oxalates and acetates of sodium, potassium, and ammonium have some stripping power.

The Theory of Chrome Tanning, etc.

Perhaps the explanation suggested by Wilson (*J. Amer. L.C.A.*, 1917, **12,** 114) marks the first step to account for chrome tanning as the result of chemical combination. In the absence of a better theory, he sees no objection to considering alum, chrome, and iron leathers as the collagen salts of triacid bases, though he states that in actual tanning there is probably first a fixation of basic salts, and to some extent a fixation of metallic hydroxide upon the hide fibres. The change which accompanies " ageing " of mineral-tanned leathers is probably due to the slow combination between the collagen and the metallic hydroxide precipitated upon the fibres, thus

$$3R\diagup\begin{matrix}NH\\|\\CO\end{matrix} + Cr(OH)_3 \rightleftharpoons Cr(NH_2 . R . COO)_3$$

Collagen. Chrome leather.
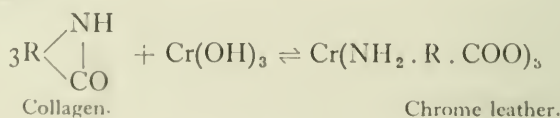
If collagen could be regarded as the anhydride of gelatin, through the extraction of one molecule of water from each molecule, and taking Wilson's value of the molecular weight of gelatin as 768,

then that of collagen would be 750.   Using this value, it is found that according to the above equation, 100 grams of collagen should combine with 3·38 grams of chromic oxide to form chromium tricollagenate, and 100 grams of gelatin should require 3·30 grams to form chromium trigelatinate.   Lamb and Harvey (*Collegium*, London, 1916, 201) state that leather containing 2·8-3·0 per cent. Cr_2O_3 was undertanned, and Lumière and Seyewetz (*Bull. Soc. Chim.*, 1903, **29**, 1077) found that 100 grams of gelatin fixed 3·2-3·5 of Cr_2O_3 from any chromium salt solution.   These observations appear to be in accord with Wilson's theory, though in the case of gelatin, Wood (*J. Soc. Chem. Ind.*, 1908, **25**, 384) could not confirm Lumière and Seyewetz's work, and stated that the amount fixed depended upon the concentration and basicity of the chrome liquor.   He found in one instance that as much as 13·6 grams of chromium oxide had become fixed, which Wilson accounts for by postulating that conditions might prevail during a reaction which would favour the hydrolysis of gelatin with the formation of more terminal amino and carboxyl groups, and thereby enable the gelatin to combine as a polybasic acid instead of as a monobasic acid. Hence the amount of Cr_2O_3 would be some multiple of 3·3, as was roughly the case in Wood's experiment.

The results of Thomas and Kelly (*Ind. Eng. Chem.*, 1922, **14**, 621) seem to support this conception ; thus the maximum amount of chromium oxide absorbed in 48 hours by hide powder was 13·4 grams for each 100 grams of protein, whereas when absorption was allowed to continue for $8\frac{1}{2}$ months, a maximum of 26·6 grams was reached.   The former is nearly four times the amount calculated by Wilson for the simple collagenate, and consequently was regarded as *Tetrachrome leather*, whereas the latter is slightly less than eight times, which therefore was an *Octachrome leather*.   On purely arithmetical grounds, Wilson's idea may be considered satisfactory, but it is not so when viewed from the chemical standpoint.   It will be remembered that collagen and gelatin act as bases, *i.e.*, with their : NH and · NH_2 groups, at pH's less than the isoelectric point, *circa* pH 4·7, and as acids, *i.e.*, with their ·COOH groups, at higher pH's.   Now, ordinary chrome tanning liquors invariably have lower pH's than pH 4·7, and in order for tanning to be the result of combination of chromium with collagen carboxyl groups, it will be necessary for the chrome collagen compound to be extremely insoluble, such that the chromium might be able to react with the infinitely small amount, if any, of ionised carboxyl groups.   Cobb and Hunt (*J.A.L.C.A.*, 1926, **21**, 454) considered that if tanning could be carried out with liquors at the isoelectric pH and above, when the dissociation

of the carboxyl groups becomes the predominating feature, increased chrome fixation should occur. They found no such increase, but observed that chrome absorption tended to become a maximum at about pH 6. In order to prepare liquors having varying pH's, they added either sodium acetate or formate in small amounts to the liquors, and added acid or alkali as required. Cobb and Hunt favour the view that chrome tanning is merely the outcome of physical adsorption on account of the large surface provided by the hide substance. This presumably would depend largely upon the sign of the electric charge carried by the collagen and the chrome. At pH's below 4·7, collagen bears a positive charge, and consequently for the coagulation of a chrome sol at the surface of collagen, it would be expected that chromium hydroxide particles would be electronegative. Actually, they may be either electropositive or electronegative, and according to Stiasny and Lochmann (*Collegium*, 1925, 200) equally good leathers can be produced with chrome liquors whose chromium hydroxide migrates to either the anode or cathode when under the influence of the current. Stiasny (*Z. angew. Chem.*, 1924, **37**, 913 ; *Gerber*, 1924, 183) attributes the loss in tanning action of chrome liquors to which addition agents, *e.g.*, sodium acetate, oxalate, and sulphite have been added, to the formation of chromium compounds in which all the so-called secondary or auxiliary valencies are saturated. Hence the ability of a chrome liquor to tan is connected with the presence of unsaturated secondary valencies, and consequently chrome tanning is the outcome of the direct attachment of collagen to a central chromium atom by means of residual valency forces whose magnitude, and also the stability of the compound formed, is a function of the composition of the internal sphere. Such a theory is probably incapable of proof.

In addition to the chromium hydroxide fixed by the pelt, appreciable amounts of acid radical from the tanning liquors are also fixed, some of which is removed by subsequent neutralisation. In the opinion of the author, chrome tanning is the result of (*a*) combination of collagen with some acid radical, (*b*) precipitation of basic chromium salt on the fibres, and (*c*) the rendering of the basic chrome salt less readily soluble by " ageing." Neutralisation of the tanned leather removes the acid in combination with the collagen and to some extent some from the deposited basic chrome precipitate.

The curve in Fig. 84 referring to the reaction of sodium hydroxide upon a basic solution, having the composition $Cr(OH)SO_4$, prepared by reducing potassium dichromate with sulphur dioxide

and boiling until the excess of sulphur dioxide was expelled, gives an idea of the type of reaction which a basic chrome liquor undergoes after penetrating into the hide. The interaction of the hydrolysed acid with the collagen causes a rapid increase in pH, and thus facilitates precipitation at the collagen interface in the form of a basic chromium salt. It is here that the proximity of the precipitation pH of chromium hydroxide to that of isoelectric collagen plays such an important *rôle*, for it is likely that the slight hydrolysis of the collagen hydrosulphate will not affect the pH to any great extent, as the hydrolysis will be suppressed through being confined within the pelt. Similar remarks apply also to alum and iron tanning. As far as the author could ascertain electrometrically, the presence of gelatin in an aluminium or chromium salt solution, whilst undergoing precipitation with sodium hydroxide does not affect the hydrogen-ion concentrations, as would probably have occurred if gelatinates had been formed. Sheppard, Sweet, and Benedict (*J. Amer. Chem. Soc.*, 1922, **44,** 1857) from hydrogen electrode titrations of gelatin to which varying amounts of alum were added, concluded that the effect of the latter was to displace the isoelectric point of gelatin to about pH 4·2. This pH, however, refers to the precipitation pH of aluminium hydroxide (*vide* page 259). Their measurements of the rigidity of gelatin containing alum at different pH's are significant in that they show that alum produces a tougher gelatin. Sheppard (*Ind. Eng. Chem.*, 1922, **14,** 1025) has recorded the effects which varying amounts of alum may have on the melting-point of gelatin. The highest melting-points were obtained when the pH happened to be that required for the precipitation of aluminium hydroxide, and they fell rapidly for pH's on either side. When precipitation was prevented within the gelatin by means of citric acid the maximum melting-point occurred at the same pH, but to a considerably reduced extent.

It is probable that these conditions also refer to chrome leather as far as its resistance to heat is concerned (*cf.* Schiarparelli, *J.S. L.T.C.*, 1925, **6,** 413). It may be that the cause of this change at and above the precipitation pH is due to the gelatin fibres, or particles, becoming encased with basic aluminium sulphate, which actually is first precipitated, and not the pure hydroxide, and that this casing becomes impaired as the pH is raised through the progressive decomposition of the basic precipitate. It would appear, therefore, that in the neutralisation of leather, great care should be taken to neutralise only to the respective precipitation pH, for chrome pH 5·3, and for alumina pH 4·1.

CHAPTER XXIII.

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATIONS IN THE VEGETABLE TANNING OF LEATHER.

THE nature of the constitution of vegetable tanning materials still remains obscure, though much has recently been done which throws light upon the subject. Perhaps the most important advance was made by Emil Fischer in 1918 in synthesising gallo-tannic acid, the tannin of oak galls. Pure organic chemical research will undoubtedly assist in the development of leather chemistry, but the results forthcoming from physico-chemical investigation are certainly of greater immediate value.

Tannins precipitate gelatin from solution, very probably through the formation of an insoluble gelatin tannate, and also adhere to the collagen present in hide in such a way that the resulting product is not decomposed by water. The actual tannins in tanning liquors are colloidal, but it is hardly permissible to state that the tanned insoluble bodies are merely colloids because they are the outcome of the physical union of two simple colloids. Chemical forces come into play, for the tannins are weakly acidic in their behaviour, and in acid solutions of hydrogen-ion concentration greater than about pH 5 collagen behaves as a base. Tanning extracts contain non-tannins which are crystalloidal and therefore diffusible and which do not combine with the proteins. Nevertheless, as Wilson and Kerr (*Ind. Eng. Chem.*, 1920, **12**, 1149) found with completely detannised liquors, the non-tannins may produce tannins on oxidation. Perhaps the view of Wilson and Kerr (*ibid.*, 1920, **12**, 465 ; 1921, **13**, 772), that tannin is that organic matter which combines irreversibly with hide substance, offers the best practical definition.

Thomas and Foster (*ibid.*, 1922, **14**, 191 ; 1923, **15**, 707) have shown by electrophoresis experiments that the different vegetable tanning materials at their natural reaction, about pH 4, migrate anodically ; in other words, they are negatively charged colloids and therefore behave as acids. On increasing the hydrogen-ion concentration the migration speeds become reduced, until at pH values between 2·5 and 2·0, the direction of the movement

undergoes a reversal. Many of the commonly used tannins thereafter suffer precipitation. The reversal is probably due to the growth of the particles to the state of hydrophobic suspension and then they adsorb hydrogen-ions, as is the case with charcoal.

A variation in the pH of vegetable tanning liquors may have a pronounced effect on their colours, and consequently on the resulting leathers. Thus Wilson and Kerr (*Ind. Eng. Chem.*, 1921, **13**, 1025), who studied the effects produced on gambier and quebracho liquors when left exposed to the air for differing lengths of time at different pH values, found that the colour changed from a light straw at pH 3 to a very deep red at pH 12. This colour-change is reversible if the liquors are acidified before they have long been exposed to air, but after a little time the liquors become darker in the more alkaline solutions and do not regain their original bright colour on bringing to pH 3. This indicator-effect accounts for the dark colour of a tanned skin from which the lime had not been completely removed, though such a colour may often be brightened if the leather is treated with acid soon after tanning.

Another observation of Wilson and Kerr on the consequences of leaving certain vegetable tanning solutions having high pH values exposed to the air, is of interest, namely, that after keeping a liquor at pH 9 for 24 hours it produced a voluminous precipitate on acidifying back to pH 3. In solutions of lower pH values this effect was considerably reduced as regards speed, and curiously enough it did not take place at all in solutions more alkaline than pH 9.

The influence of hydrogen-ion concentration, the concentration of the tanning liquors, and the time allowed for tanning has been very carefully investigated by Thomas and Kelly (*Ind. Eng. Chem.*, 1923, **15**, 1148), using hide powder and six different tannin extracts, *viz.*, quebracho, gambier, hemlock bark, oak bark, larch bark, and wattle bark. To ascertain the amount of tannin fixed, they adopted a method introduced by Wilson and Kerr (*loc. cit.*), based on the definition of tannin given above. The determinations simply involved the measurement in the increase in weight of a sample of hide powder, after tanning and thorough washing in order to remove the non-tannins. The curve marked " tanning liquor " (Fig. 85) expresses the general nature of their results, though, of course, the shape was effected by the particular tannin extract used, its concentration and the time of tanning. Thus with a prolonged time of tanning, there was a tendency for the minimum at pH 5 to disappear. It will be observed that the curve is similar to the swelling curves of collagen and gelatin. The minimum

fixation will be seen to have occurred at pH 5, which is approximately the isoelectric point of collagen. The curve shows that an increase in the fixation of tannin occurred from pH 5 to pH 2 ; a fact which is in harmony with the acid nature of the true tanning agent. It is difficult, however, to visualise why tannin should have been fixed on the alkaline side of the isoelectric point. Wilson and Gallun (*Ind. Eng. Chem.*, 1923, **15,** 71) found, in investigating the plumping of calf skin at 7° C. in regard to the concentration of hydrogen-ions, that there were two minimum points of plumping, at pH 5·1 and pH 7·6. To explain this they suggested that these two minima represent the isoelectric points of two different forms of collagen. If, therefore, it be assumed that

the pH range 5·1 to 7·6 corresponds to some internal rearrangement from the ordinary form, whose isoelectric point is at pH 5, to another having pH 7·6 as its isoelectric point, then tannin fixation above pH 5·0 must be attributed to combination with the second form. (See, however, Fig. 81.) This explanation should be taken with reserve.
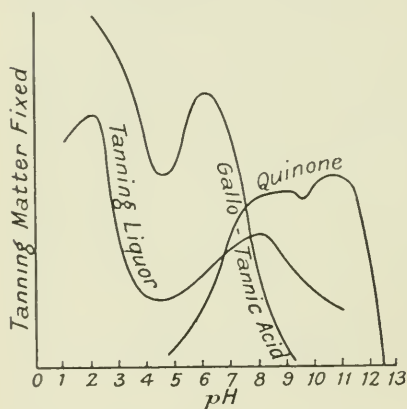
FIG. 85.—Variation with pH of Tannin fixed by Hide Powder.

Vegetable tanning extracts contain organic matter of the nature of quinone, and moreover, certain non-tannins on oxidation by the air give quinone-like substances in alkaline solutions. Such bodies have tanning action. Thomas and Kelly (*Ind. Eng. Chem.*, 1924, **16,** 925) have studied the rate of tanning with benzo-quinone at different pH values. The curve marked " quinone " in Fig. 85 illustrates their results and shows that the tanning action of quinone comes into play above pH 6.

It might be concluded that the presence of quinone derivatives in the tannin extracts would supply an adequate explanation of the tanning at pH values higher than 5, but in another paper by the same workers (*Ind. Eng. Chem.*, 1924, **16,** 800) it has been demonstrated that tannic acid, which was rendered free from quinone-like substances, and also reasonably free from non-tannins, still was able to produce an increased tannin fixation in the region of pH 7. The curve labelled " gallo-tannic acid " depicts their

results, from which it appears that tannic acid fixation as such is not possible above pH 9.

Gordon and Gilman (*J.I. Soc. Leather Trades' Chemists*, 1927, **11**, 213) have directed their attention to the importance of hydrogen-ion concentration in vegetable tanning, and in order to obtain results which reproduce practical tannery conditions more satisfactorily they used partially delimed ox-hides and a tanning liquor composed of a blend of Valonia, Myrabolams, Mimosa bark, and chestnut extract, which blend is similar to that commonly used in English tanyards. They estimated the total amounts of tanning matter which had been absorbed after the hides had undergone different periods of tanning. Their results are given in Fig. 86, in which the numbers correspond to the number of days of tanning. These curves do not represent the true degrees of tannage, for considerable proportions of non-tannins are included. The broken curve gives the true degree of tannage after 42 days, whereas the top curve gives the apparent tannage in the same time.

The curves show an increased tannin fixation when the liquors were about pH 2. Gordon and Gilman, however, found the resulting leather to be of little commercial value as it was harsh and brittle and had
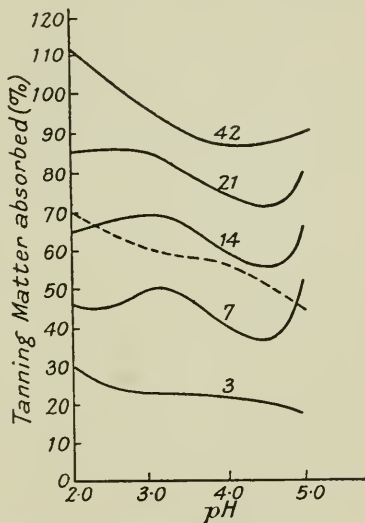
FIG. 86.—Variation with pH of Vegetable Tanning Matter (Tannin and Non-Tannin), absorbed by 100 parts of Partially Delimed Ox-hide.

an unsatisfactory colour. When tanned at pH 2·5 the leather was found to be firm and was not brittle, though its colour was not all to be desired. Their results show that tanning at pH 3 gave rise to a leather which appeared to have the properties most desired in sole leather, *viz.*, firmness without brittleness, good substance and colour, and a fairly high percentage of tannin. The increase in pH had one disadvantage in that it tended to promote " bloom " deposition, and this appeared on the leather in question. The samples tanned at pH 4·0 and 5·0 had heavy deposits of " bloom," though both leathers were mellow and of good colour.

As regards the suggestion of Thomas (*J. Amer. L.C.A.*, 1926,

21, 513) that the best results would probably be obtained by tanning at a pH in the neighbourhood of the isoelectric point, *i.e.*, 4·5 to 5·0, so as to secure better penetration of the tanning liquors and then to increase the tannin fixation and the plumping of the hide by lowering the pH of the tanning liquor to pH 3, Gordon and Gilman point out that it is a matter for further investigation as to whether any very marked plumping would occur once the pelt is struck through.

The part played by hydrogen-ion concentrations in vegetable tanning has also been investigated by Pawlowitsch (*Collegium*, 1928, 2).

CHAPTER XXIV.

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATIONS IN SUGAR MANUFACTURE.

THE regulation of the acidity or alkalinity of the various sugar solutions during the purification processes involved in the manufacture of sugar has always been a problem of paramount importance. Until quite recently, it was customary to investigate it only in terms of the titres obtained when the juices were titrated with either alkalis or acids in presence of the commoner indicators. Though such a method undoubtedly provided data of value for the purpose of control, especially when the juice or beet employed in the particular refinery was obtained from one special source and the initial solutions were of an approximately constant concentration of the non-sugars, the data, however, became of little technical use when raw materials obtained from different sources were compared, and led to unsatisfactory results when attempts were made to use them to standardise the processes adopted in different manufactories. The variable acid contents, inorganic and organic, in sugar juices gave rise to different titratable acidities, which very often, due to the varying buffering effects of the several acids, were not in any way comparable with the hydrogen-ion concentrations of the solutions, on which it is now known that the efficiency of refining is very largely dependent. The recognition of the real meaning of *true acidity* is to be seen by the increasing number of references to the use of electrometric and colorimetric methods for the determination of hydrogen-ion concentrations in both research and process work. The application of the measurements of hydrion concentrations as a powerful method of control is only just becoming to be realised, though in some refineries, particularly in America, it is now being generally adopted. The following discussion will show how essential correct pH control is, and it appears certain that as sugar refining becomes more and more scientific, such control will be held in greater esteem than it is to-day.

Before dealing with the part played directly by hydrogen-ions, it will be necessary to consider for a moment some of the principles underlying sugar manufacture. Sugar refining is essentially a process of fractional crystallisation from liquors which are more or less impure. It is well known that crystallisation may be very considerably influenced by the presence in the mother-liquor of substances which are colloidal in nature. The dispersed particles sometimes have an impeding effect upon crystallisation, and when it once has taken place the colloidal particles often contaminate the crystals in such a way that the impurities are not easily removed. The important problem then is the efficient purification of the liquors from which sugar crystals are eventually to be obtained. Hence the need of knowing at the outset the composition of the solutions and juices.

The juice squeezed out of sugar canes by milling comprises the sugar sap, the soil water, and protoplasm, the proportions of which depend upon the pressure exerted between the rollers. The sucrose content of the canes varies from 11 to 16 per cent., which happens to be about the same amount as that of the fibre, or *bagasse*. According to Heriot (*The Manufacture of Sugar from Cane and Beet*, London, 1920), a typical analysis of an undiluted cane juice is : Water, 83·0 per cent. ; sucrose, 15·0 per cent. ; reducing sugars, 1·0 per cent. ; organic non-sugars, 0·5 per cent. ; and mineral matters, 0·5 per cent. Such a juice is 17·0° " Brix," *i.e.*, the sum of the percentage amounts of solutes and the " purity " of the sugar is $15/17 \times 100 = 88·2$ per cent. The reducing sugars, namely, those which reduce Fehling's solution, are glucose and fructose. The organic non-sugars include such acids as glycollic, malic, oxalic, succinic, tannic, and from diseased canes, acetic. They also include certain nitrogen compounds, some of which are distinctly colloidal, *e.g.*, albumin, albumoses, amines and amino-acids, nucleins, peptones, etc. ; colouring matters, *viz.*, anthocyan, saccharetin and chlorophyll ; and other substances as pectin and gum (xylan). The mineral matters which account for the ash are derived from the soil and contain phosphates, chlorides, sulphates, nitrates, silicates of aluminium, iron, calcium, magnesium, sodium, and potassium. Anthocyan is the dark colouring matter in the rind of purple canes, and is both difficult to remove completely and to bleach with sulphur dioxide in the course of sugar manufacture. Saccharetin, though colourless when acid, becomes bright yellow in alkaline solutions, and is regarded as the cause of the colouring of the so-called " Demerara sugar." Though it cannot be precipitated with acids or alkalis, it can be bleached with sulphur dioxide. That

tannins and polyphenols are sometimes found in sugars may be concluded from the greyish tinge which they assume, and especially is this the case when iron vessels have been used. To prevent inversion of the cane sugar from taking place when the juice is concentrated by boiling, it must not contain any acid, and milk of lime is therefore added until the juice has just become alkaline. This causes some non-sugars to be precipitated. Calcium oxalate is also thrown out of solution as " scales " and so too is some little of the phosphoric acid as the calcium salt. Care here is necessary to avoid too great an alkalinity or it will cause the decomposition of any reducing sugars with the production of the calcium salts of lactic, glucinic and saccharinic acids. Calcium salts of acetic, glycollic, succinic and malic acids should be avoided in the juices, for if they are allowed to pass into the molasses adhering to the raw sugar crystals, will, being hygroscopic, cause the crystals to become moist and so reduce their commercial value. On the other hand, certain bacteria flourish in cold alkaline juices which convert the sugar into the gummy substances, dextran and levan, and lactic and acetic acids. Acidity, such as may be produced by the latter, will in time kill these organisms.

As the composition of the original sugar solution obtained from sugar canes is determined to some extent by the manner in which the milling is effected, so, too, in the beet industry, is the initial solution dependent upon the process of diffusion into water of the juices contained in special types of beets after they have been cut into slices. If no cells were cut open in the act of slicing then the diffusates would be chiefly crystalloids, the colloids, such as the albuminoids, being unable to pass through the cell-walls. Actually, some albuminoids contained in the fractured cells do pass into the diffusion juice, many of which become coagulable on heating. The sucrose content of sugar beets ranges from 12·7 to 16·5 per cent., and the amounts of reducing sugars are considerably lower than in cane juice. The diffusion juice is often opaque, grey, or yellowish in colour, darkens readily in air, and has a specific gravity of from 1·048 to 1·063 (*i.e.*, 12° to 15° Brix.). It contains from 10 to 14 per cent. sucrose, 0·4 to 1·7 per cent. of organic non-sugars, and 0·3 to 0·6 per cent. of mineral matters. The organic acids in beet juice differ somewhat from those in cane juice, the following having been found to be present : aconitic, citric, glycollic, malic, oxalic, succinic, and tartaric. Phosphates, sulphates, nitrates, and silicates are also present. Besides the usual protein derivatives, catechol, which in conjunction with iron salts provide some of the colouring agents, cholesterol, glucosides, pectins, pentonsans, lecithin are often to be found. Condensation

products of amino-acids and reducing sugars give rise to some of the colouring. The mineral matters are similar to that in cane juice. Much of the colour of sugar juices, which are not bleached by sulphur dioxide treatment, can be removed by treatment with bone-chars which act as adsorption agents.

Not only are the sugar crystals affected by the adhesive coatings of molasses, but the " grain " of the crystals themselves is to some extent determined by the insoluble matter in the juices ; the incorporation of insoluble material in the crystals tending to make them small and unsatisfactory. A considerable proportion of the molasses which contaminates the raw sugars obtained from the initial concentration can, if of satisfactory grain, be removed by the process known as " affination." Thus, raw sugars, separated by means of centrifugal filtration, may be as much as 96 per cent. pure when obtained from mother-liquors or molasses, whose purity vary from 65 to 75 per cent. Such crystals and molasses may be obtained from raw juices which before boiling were from 80 to 88 per cent. purity. It is legitimate, therefore, to assume that crystals so prepared having 96 per cent. purity would be composed of almost pure sugar, say, 99 per cent. purity, and a little molasses constituting a skin of about 70 per cent. purity. It so happens that the molasses or syrups of low sugar contents, but with comparatively high contents of non-sugars, *i.e.*, syrups of low purity, can be obtained, which constitute solutions saturated with respect to sucrose but which are unsaturated with respect to nonsugars. Hence, these solutions, though unable to dissolve more sucrose, will still be able to dissolve non-sugars, a property which is taken advantage of in the process of affination. The raw sugar crystals are therefore subjected to treatment in suitable mixers, " minglers," with suitable low-purity syrups which extract much of the impurities. Incidentally these syrups become high in non-sugar content, and in order to use them for the production of sugar crystals they must undergo rigorous and carefully controlled chemical treatment so as to precipitate as much of the non-sugars before further crystallisation of sugar is attempted.

The remaining part of this chapter will be devoted to the chemical methods which are employed for the purification of sugar solutions. It was stated earlier that some little calcium phosphate underwent precipitation when the acidity of the milled cane juices was adjusted by the cautious addition of lime cream. The amount of phosphoric acid thus removed, however, is negligible when compared with that left in solution, and consequently that part of the process cannot be considered to have any refining value. Sugar juices, to which the non-sugars have been translocated by

means of the affinating process, undergo one or more of the following treatments : *defecation*, *sulphitation*, and *carbonation*. For the manufacture of raw cane sugar either " defecation " or " neutral-sulphitation " is employed, whereas for white cane sugar both acid-sulphitation and carbonation are often adopted. The chemical treatment given to beet juice is usually carbonation which is very often carried out in two stages, though this procedure is sometimes combined with one of sulphitation. It should be mentioned here that when sulphitation is applied prior to carbonation, the calcium precipitate is so gelatinous that it becomes very difficult to manipulate.

Defecation.

Defecation is a process by which the sugar juices are clarified by the addition of slaked lime in such quantities as to cause the maximum precipitation of calcium phosphates in the flocculent condition. There are limits to which liming can be safely conducted, for if too high pH's are attained the " invert " or " reducing " sugars will undergo decomposition on boiling. The physical condition of the phosphate precipitate causes it to adsorb part of the colloidal impurities, but the amount actually carried down depends upon the amount and nature of the precipitate produced. Ordinarily, this is determined by the quantity of phosphoric acid in the juice, and in cases where it is found to be insufficient, phosphoric acid is sometimes added to the juice.

The precipitation of calcium phosphate has been the subject of much recent research on account of its importance in analysis, agriculture, calcification in the animal body, and in sugar refining. Britton (see page 325) has investigated its precipitation with calcium hydroxide from aqueous solutions of phosphoric acid, and also from acid solutions containing sucrose. When precipitation was carried out at 20° C., it was found that a precipitate did not begin to appear until pH 6·7 had been attained and 1·5 equivalents of lime water had been added. The variation in hydrogen-ion concentration was similar to that shown in Fig. 87, which gives the pH neutralisation curves of phosphoric, sulphurous, and carbonic acids. The greater parts of these curves will be unaffected by the concentration of acid taken except the first halves of the sulphurous and phosphoric acid curves and the last portion of the carbonic acid curve. They have been drawn for M/100-acid solutions. By comparing the curve given in Fig. 41 for calcium hydroxide with that using sodium hydroxide, it will be seen that much of the delay in precipitation was

due to the tendency for the normal neutralisation pH change on adding lime to be followed, thus saturating the solution with respect to calcium phosphate. It was calculated, however, if time be allowed for the attainment of equilibrium that calcium phosphate should begin to separate at pH 5·5. Sucrose had very little effect as far as hydrogen-ion concentration was concerned. Farnell (*J. Soc. Chem. Ind.*, 1926, **45**, 343T) studied this problem more particularly from the point of view of the sugar refiner and found that when boiling was carried out a pH of about this order was necessary. An examination of the muds obtained from juices which had been limed to neutrality to phenol-phthalein, pH 8·4, by Paine and Balch (*The Planter and Sugar Manufacturer*, 1927, **78**, 127, 148) revealed that 20 per cent. of total mud was mineral matter.

FIG. 87.—Titration Curves of Carbonic Sulphurous and Phosphoric Acids.

According to Bond (*Internat. Sugar Jour.*, 1925, 311) such an ash contains principally the phosphates, calcium, iron, aluminium, and magnesium. Iron and aluminium are exceedingly difficult to remove as hydroxides, owing to the protective effect which sugar has upon them in retaining them in a comparatively stable colloidal solution. Hence it appears that if the sugar juice does not contain sufficient phosphoric acid to enable the iron to be precipitated the iron will have a deleterious effect upon the colour of the juice should any polyphenols be present. The organic nonsugars which are thereby eliminated from the juice constitute about 80 per cent. of total nitrogen compounds, *e.g.*, albumin, and very small percentage amounts of anthocyan and pectin, and no cane gum. The amount of non-sugars removed from the juice depends

to some extent upon the bulkiness and nature of the calcium phosphate precipitate, but on the average the amount so obtained is only about 11 per cent. of the total present. The juice, however, becomes transparent and yellow, and its purity increases by about one unit. The amount of calcium phosphate obtainable is also dependent upon the pH value to which liming has been carried out. The maximum pH for defecation is restricted to pH 8·25, for at this stage Bomonti (*Report Assoc. Hawaiian Sugar Technologists*, October, 1926) has found that the destruction of reducing sugars first becomes evident.

From the chart, Fig. 88, which gives the various pH's at which precipitations encountered in sugar refining begin to take place and also the pH ranges within which inversion of cane sugar occurs and the invert sugars become converted into acids, it will be seen that the pH range available for defecation is from just below pH 7 to just above pH 8. (It should be mentioned here that the pH's at which tricalcium saccharate and certain non-sugars given in Fig. 88 is approximate only.) Bomonti, however, states that the maximum increase in purity of cane juice is generally secured when liming is carried up to pH 8·3 to 8·5, at which alkalinity the amount of decomposition of the reducing sugars is negligible. As Paine and

FIG. 88.—pH Chart of Chemical Processes in Sugar Refining.

Keane (*The Planter and Sugar Manufacturer*, 1927, **78**, 168) point out, not only the pH, but also the phosphoric acid content of the juice should be controlled. Smith (*Report Hawaiian Sugar Planters' Assoc.*, 1924) states that it seems impossible to obtain a clear limpid juice if the P_2O_5 content is below 0·02 per cent., and McAllep and Bomonti (*Hawaiian Planters' Record*, 1922, **26**, 122) conclude that if 100 c.c. of juice contain more than 0·03 gram P_2O_5, clarification becomes easy, whilst if there is less than this amount the juice will be dim, the massecuites may boil slowly, and the raw sugar

produced in the refinery may filter slowly. Farnell (*loc. cit.*) found that at least 0·005 to 0·01 gram P_2O_5 must be present in 100 c.c. in order that calcium phosphate may be precipitated to such an extent that it will adsorb part of the colloidal impurities. He suggests that the addition of phosphoric acid to certain poor juices may subsequently become economic. A great advantage of a high phosphoric acid content is that it will cause increased precipitation at a lower pH, which will promote good clarification by removing a greater proportion of colloidal matter and non-sugars and at the same time keep the pH well within the limits necessary to avoid inversion and destruction of reducing sugar. Moreover, the unprecipitated phosphoric acid will exert a suitable buffer action.

It should be mentioned that the pH measurements are usually made on juice diluted to 15° Brix (15 per cent. solids), whereas the pH's with which the refiner is mainly concerned are those prevailing when the solutions become concentrated to 50° Brix (say) by heating. Walton, McCalip, and Hornberger (*Ind. Eng. Chem.*, 1925, p. 51) observed that whenever the quinhydrone electrode was used to determine the pH of samples of syrup higher than 40° Brix, the value found was always lower than that of the same sample when diluted to 15° Brix. A typical difference is a variation from pH 6·36 for a 46° Brix syrup to pH 6·61 after it had been diluted to 15° Brix. This should be borne in mind in the factory, or inversion may occur in the concentrated juice through commencing with too low a pH. Heating alone produces a diminution in the pH of limed juices, which may be due to the precipitation of calcium phosphate and the consequent buffer action of the phosphate left in solution.

Sulphitation.

The clarifying effect of sulphitation lies in the adsorption by calcium sulphite precipitates of colloidal matter and soluble non-sugars. The process may be carried out in either of two ways : (*a*) lime cream may first be added to give a high pH, causing the juice to become very dark on heating, but giving a more complete precipitation of calcium pectate, anthocyan, and gum, and then the lime is neutralised by passing in sulphur dioxide to a pH which will bring about the maximum precipitation of calcium sulphite without any decomposition of sugar ; or (*b*) to render the juice strongly acid by passing through sulphur dioxide and then liming to a desired pH. As is well known, sulphurous acid does not bleach in alkaline solutions, and therefore the first method, *viz.*, *neutral-sulphitation*, is only applicable for the manufacture of raw

sugar, and the second method, "*acid-sulphitation*," for white sugar. The amount of sulphur dioxide added in method (*b*) varies from 0·6 to 2·5 grams per litre. After liming, the juice is heated to 100° C. and then run into tanks to enable the calcium sulphite and phosphate to settle. In Java the raw juice is heated to 80 to 85° C. and then " sulphited " and limed simultaneously, a process which is said to give better precipitation.

The *p*H change undergone when a solution of sulphur dioxide is reacted upon with an alkali is given in Fig. 87. Unfortunately, neither the hydrogen, nor the quinhydrone, nor the oxygen electrodes can be used for this purpose, and one is compelled, therefore, to resort to colorimetric methods with indicators. The curve was constructed for 100 c.c. of $M/100–H_2SO_3$ solution with $N/10–$ NaOH from the dissociation constants recorded in the literature, *viz.*, $K_1 = 1·74 \times 10^{-2}$ and $K_2 = 1 \times 10^{-7}$ (Kolthoff, *Chem. Weekblad*, 1919, **16**, 1154). The buffered curve produced by the addition of the second equivalent of alkali is almost independent of the concentration of the acid. Slaked lime first reacts with a sulphurous acid solution to form a soluble salt, $Ca(HSO_3)_2$, over a *p*H range up to about *p*H 5. This range, incidentally, is that at which inversion can occur, and therefore the lime should be added as quickly as possible, and also in the cold. Farnell (*J. Soc. Chem. Ind.*, 1925, **44**, 530T) has investigated the *p*H at which calcium sulphite begins to precipitate, and found that at 20° a precipitate began to separate when 1·1 equivalents of calcium hydroxide had been added and a *p*H of 5·5 had been reached. Precipitation thereafter occurred with increasing *p*H, 95 per cent. having separated at *p*H 7·4 and 100 per cent. at *p*H 9·2. When the solutions were mixed at 20° and then boiled, cooled and the *p*H determined, precipitation still occurred with 1·1 equivalents of calcium hydroxide, but at *p*H 5·2 ; 95 per cent. being precipitated at *p*H 7·0, and 100 per cent. at *p*H 8·8. Sugar had no retarding influence, but diminished the size of the characteristic clusters of crossed needles of $CaSO_3,2H_2O$. Colloids, however, retarded precipitation, and caused the calcium sulphite to separate as spherical granules, whose size increased with temperature, time, *p*H and initial concentration of sulphurous acid. He found that the greater the amount of sulphur dioxide used the more complete was the precipitation of calcium sulphite on liming back the hot juice to a given *p*H. Farnell states that *p*H 6·8 is the figure employed in the white sugar factories of Natal and Mauritius. Though *p*H 8·6 for the hot juice is ideal as far as obtaining the optimum sulphite precipitation is concerned, the alkalinity is such as would make the juice somewhat dark in colour. This

renders such a pH unsuitable for white sugar manufacture, but for the production of raw 96 per cent. sugar this is not so serious ; in fact, McAllep (*Intern. Sugar Jour.*, 1925, **27,** 382) has recommended pH 8·2 as corresponding to the best hydrogen-ion concentration of the hot juice on leaving the settling tanks in the Hawaiian factories. Farnell advocates liming to pH 7·6 to 7·8, at which sulphite precipitation would more nearly approach completion.

Carbonation.

Purification by carbonation comprises the addition of lime-cream to the sugar solutions in large excess, followed by the passage through them of carbon dioxide until a pH is reached which will not allow the precipitated calcium carbonate to pass back into solution as the bicarbonate. The pH variation given in Fig. 87 for the neutralisation with NaOH of carbonic acid, which happens to be almost independent of concentration of reactants except at the two ends, the dotted lines referring to more concentrated solutions of alkali, gives some idea of the pH change undergone in sugar solutions. The use of calcium hydroxide will produce a difference in pH during the neutralisation of the second half of the acid, due to precipitation, but not during the first half. From Johnston's (*J. Amer. Chem. Soc.*, 1915, **37,** 2001) data regarding the solubility of calcium carbonate in water in equilibrium with varying partial pressures of carbon dioxide, it has been calculated that for partial pressures of carbon dioxide ranging from 0·0002 to 0·0005 atmospheres the pH of the solution in equilibrium with solid calcium carbonate varied from 8·4 to 8·1. As these pressures compare with those of carbon dioxide present in the air, it follows that these pH's are those at which calcium carbonate begins to precipitate. Assuming the sugar to have no effect on this pH it appears that carbonation must not be continued below pH 8·1 otherwise the precipitate will begin to redissolve. The pH range for magnesium carbonate for the same pressures is 9·6 to 9·5. Fig. 88 shows that pH 8·1 falls almost within the limits between which these processes should be effected. Sometimes carbonation is performed in two stages by restricting the first stage to between pH 11 and 12 so as to precipitate and remove by filtration such non-sugars which tend to redissolve at lower pH's, *e.g.*, anthocyan, pectins, and gums. Care, however, should be taken to avoid the elimination of sugar as tri-calcium saccharate, $3CaO,C_{12}H_{22}O_{11}$, which, though difficultly soluble in strongly alkaline solutions, will, if given time, redissolve.

Automatic pH Recording and Control.

Some reference will now be made to the ingenious methods which have recently been developed for automatic pH reading and also for the adjustment of the alkalinity of sugar solutions. Balch and Paine (*Planter and Sugar Mfr.*, 1925, **75,** 347 ; *Intern. Sugar Jour.*, 1926, **28,** 425) found that for pH work a tungsten electrode in presence of manganic oxide worked satisfactorily in alkaline solutions. Such an electrode was found by Parker (*Ind. Eng. Chem.*, 1925, **17,** 737 ; U.S.P. 1,513,558/1924) to be capable of giving voltages when compared with a standard calomel electrode which could be calibrated in terms of pH (see page 85).

Fig. 89 shows the arrangement used by Balch and Paine. The upper portion was a calomel electrode and the lower portion, into which dipped the saturated potassium chloride " salt bridge " and also the tungsten electrode, was the electrode chamber. The latter was made of a glass tube, coated at the lower end with Mn_2O_3 around which a tungsten wire was wound, one end being passed through the glass tube containing mercury. Both electrodes were connected with a recording potentiometer. Through the electrode chamber the sugar

FIG. 89.—Tungsten and Calomel Electrodes.

solution was pumped, its temperature having previously been regulated by means of cooling coils. This apparatus could be made to give not only a continuous pH record during liming, but also warning, by lights or bells, when the pH value was not within the prescribed limits ; and by operating an electromagnetic valve, could be made to control the rate of lime addition (see also Parker, *Ind. Eng. Chem.*, 1927, **19,** 66).

pH Survey of Sugar Cane Soils.

O. Arrhenius (*Java Archief*, 1927, **35,** 503) gives an interesting account of the methods adopted in the survey of the sugar-cane fields of Java with regard to the hydrogen-ion concentration of the aqueous soil extracts. Sugar canes thrive best in soils of about

pH 7, and consequently a systematic investigation of the soils has been made in order that only those areas having suitable pH's should be used, it being uneconomic to correct, by adding lime, those soils which are more acid.   Sampling is a matter of considerable importance, and for each test about 300 grams of soil were taken, placed in a muslin bag, dried, and after transference to bottles, were extracted with water and the pH estimated by means of Gillespie's " Drop Ratio Colorimetric Method."

CHAPTER XXV.

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATIONS IN PULP AND PAPER MANUFACTURE.

THE production of satisfactory paper depends on the efficient adjustment of the hydrogen-ion concentrations of the liquors employed. This applies more particularly to the sizing operations.

Much of the failure of manufacturers to realise that the acidity of the liquors should be controlled to a higher degree of precision than that obtainable by means of litmus, and very often by litmus papers, is shown by a certain lack of uniformity in the different batches of paper which have been manufactured in apparently the same way. Thus printers find that their type and plates deteriorate more readily when used on some papers than on others, although all were purchased as of the same quality. The cause may generally be traced to the acid content. Such material, besides being of inferior quality, must have been subjected to treatment with too large a quantity of aluminium sulphate, some of which must therefore have passed out into the " backwater " and so have been lost. On the contrary, if too little aluminium sulphate be used there will be a tendency for some rosin size to remain undecomposed, and this again will lead to uneconomic manufacture. That litmus should have been selected by paper makers as the indicator for controlling the acidity of sizing solutions is somewhat remarkable, though not surprising, for, as will be shown later, its colour-change corresponds roughly to the pH range in which lies the smaller range necessary to secure good sized paper. The recent and precise methods for the determination of hydrogen-ion concentrations furnish means by which the acidities can be maintained within the narrower limits, now known to be imperative if the best papers are to be made, and incidentally limits which enable production to be carried out in the most economic manner, waste of aluminium sulphate and of rosin size being reduced to a minimum. In spite of this, it is felt that these methods are not being adopted as readily as they should be, probably due to some idea in the minds of paper manufacturers that they are uncalled for and are best left in the hands of

physical chemists. It is probable, when printers come to realise how much of the efficiency of their work and how much the wear of their type depend upon the acidity of the paper they employ, that they will include pH in their paper specifications. Another well-known disadvantage of acid paper is the decomposition and discoloration which occurs with age.

We shall now consider the various stages of paper manufacture, in so far as they lend themselves to pH control, and point out why such control appears to be necessary.

The first stage is to isolate the cellulose fibre from the raw material, namely, rags, esparto, various kinds of straw, coni-ferous woods, such as pine, spruce, poplar, and waste products, $e.g.$, paper, textiles, and jute bags, and then to convert them into pulp, sometimes known as " half-stuff." The preparation of pulp from either of these materials involves treatment with alkalis, sodium hydroxide or lime, of various concentrations, at different temperatures and usually under pressure. Linen and cotton rags, being of fairly pure cellulose, only require thorough washing by boiling with alkali and, when necessary, special treatment with malt to hydrolyse any starch which they may contain. This treatment, however, is not without its disadvantages, for it tends to soften the surfaces of the fibres and moreover to cause the pre-cipitated ferric hydroxide and calcium carbonate to become embedded in the rags. Treatment with a slight amount of acid will dissolve out this foreign material, and at the same time slightly harden the surfaces of the rags. Too much acid effects too great a hardening, and unless the hydrogen-ion concentration of the liquors is suitably regulated such treatment may lead to disastrous results. The rust encountered comes from the iron in pipes and machines.

In recent years wood has become the most important source of raw material for the paper industry, and, indeed, also for its allied industry—that of artificial silk. Pine, spruce, and poplar woods are used. The lignified fibres of which they are composed, on being subjected to alkaline hydrolysis, undergo decomposition, the first material to become soluble being the non-celluloses ; and if the hydrolytic reaction be protracted the cellulose, which con-stitutes the cell-structures, also decomposes and then dissolves. After the removal of the bark, the wood is cut up into portions as small as possible so as to provide the maximum surface to enable the thorough penetration of the liquors. Two processes are available for the conversion of these chips into pulp : (a) the soda process, and (b) the sulphite process, the latter being more widely practised. In the " soda process " the chips are boiled

with 6 to 8 per cent. NaOH under pressure. Sodium sulphate is introduced which eventually becomes reduced to sulphide by means of the extracted organic matter.

Sulphite Pulp Process.

The " sulphite process " is of considerable importance, and though it involves the use of comparatively acid solutions, which render pH control difficult, it is surprising to find that recent investigations show that, providing the chips have had a satisfactory pre-treatment, the regulation of pH enables a more uniform and satisfactory pulp to be obtained. The process comprises the action of magnesium or calcium bisulphite liquors, saturated with sulphur dioxide, at a temperature somewhat above 100° C. and under pressure for many hours. The principle underlying the sulphite process appears to be the attack of bisulphite on the ketone groups present in the lignones, which renders the ligno-celluloses soluble. Neutral sulphites have a feeble hydrolysing effect, but it does not become appreciable unless higher temperatures are employed.

Hagglund (*Papier-Fabrikant*, 1926, 24 ; 1927, 24A) points out the great part which acidity plays during cooking. Escourrou and Carpentier (*Chimie et Industrie*, 1927, **18,** 13) have made a thorough study of the subject, and reference will now be made to their results. They consider that for the treatment of resinous woods pH measurements become of great importance. The initial absorption of the sulphite should be as complete as possible, and as it is primarily an adsorption process at the surface of the wood, before any reaction can ensue, the surface must be made as large as possible by cutting up the wood into the smallest sticks. The liquors should have penetrated thoroughly into the wood before 120° C. is attained. The value of a knowledge of the pH of the sulphite liquors, which can be found with indicators, will be apparent from Fig. 90, constructed from Escourrou's and Carpentier's data. The two upper curves give the courses followed by the hydrogen-ion concentrations of the liquors during 21 hours of cooking, the pressure being gradually increased during the first 6 to 8 hours to 4 kg. and thereafter maintained approximately at this pressure. Curve U is typical of the variations undergone in the production of unbleached pulp, whereas B represents the more careful control necessary to yield a pulp suitable for bleaching. The lower curves *u* and *b* give the temperatures (right-hand ordinate) attained during the runs corresponding to U and B respectively. The first sections of U and B correspond to the impregnation of calcium bisulphite liquors into the wood

which, as the lower curves show, is accompanied by a steady rise in temperature. The slower the rate of impregnation before 120° C. is reached permits of better disincrustation and also of the liberation of rose-coloured sulphonic acids on drying which are more susceptible to bleaching than those produced at higher temperatures. The lower the pH during impregnation, though it promotes a slower action of the liquors, leads to a better product and one which is easy to bleach. If the pH, however, is kept too low the liquors may become black, to result ultimately in a serious diminution in the yield of cellulose. The downward slope of both curves which followed, showing that an increase in hydrogen-ion concentration occurred in the solutions, was due to the ap-
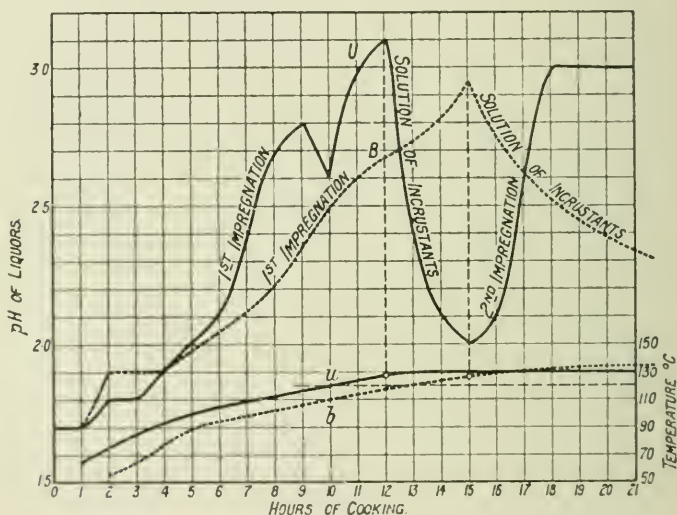
FIG. 90.—pH and Cooking of Sulphite Pulp.

pearance of organic acids in the liquors through the dissolution of the lignified matter or incrustants. The temperature curves indicate that this solvent action started at a temperature a little below 130° C. Curve B shows a regular disincrustation attended by a progressive lowering in pH. After 27 hours' cooking, the pH of the escaping liquors had fallen to 1·8, and the pulp then obtained was soft and easily bleached. This appears to be usually the case. If the pH is above 2 the pulp is found to be hard, becoming harder with increasing pH, so that it can be bleached only with difficulty ; it is therefore put on the market as unbleached quality. If the impregnation is not thorough at the beginning, which can be ensured by suitable regulation and control of the pH of the

sulphite liquors, then the solution of the non-celluloses is partial, and in the course of cooking another impregnation action is set up, as was the case in curve U. The pulp corresponding with the top of the second impregnation curve is of " unbleached " standard.

Bleaching.

Except for the lower grades of " newsprint," and the pulp designated for " browns," " wrappings," cardboards, etc., further drastic chemical treatment is given to the pulp. The process which has to be undergone by the wood and esparto " half-stuff " necessary for the manufacture of better-class papers, is one of bleaching. The " bleach " comprises, as a rule, a solution of bleaching powder, but on account of its slowness in bleaching, the bleaching liquor is very often rendered slightly acid by the addition of small amounts of dilute sulphuric or hydrochloric acid. This acid treatment is one which can be overdone ; thus too much acid will cause the evolution of chlorine, and also may convert some cellulose into oxy-cellulose which in impairing the fibre structure reduces the ageing properties of the resulting paper. Furthermore, bleaching action, being essentially one of oxidation, will tend to liberate acids by the interaction with the non-cellulose matter remaining in the wood-pulp, and if the amount of acid becomes too great, will cause the lignone groups to become chlorinated. Such chlorinated derivatives in the paper are highly deleterious. One advantage of having an acid-bleach, in addition to its enhanced efficiency, is that it dissolves out any insoluble calcium salts, e.g., calcium carbonate. Another method of preparing the acid-bleach employed in recent years has been to pass chlorine into the alkaline pulp beyond the requirements of neutralisation. This is a process, therefore, which demands careful investigation. There is no doubt that the addition of alum to the alkaline bleach, often used as a " brightening agent," is in effect an attempt to use an acid-bleach which shall be without the attendant ill-effects of an acid-bleach which contains too much free acid. As will be seen later, such a reagent tends to fix automatically the optimum acidity at about pH 4. This is probably a safe limit, but there is a probable disadvantage of aluminium hydroxide being precipitated within the pulp. Some weak acid whose dissociation constant is about 10^{-5} might prove useful, e.g., acetic acid. The use of " antichlors " should be avoided, e.g., sodium thiosulphate or sodium bisulphite, which though eliminating the chlorine as neutral chlorides may cause acids to be set free which will destroy the

wires of the machines. It is preferable to wash the pulp free from bleach-liquors, or to use *neutral* sodium sulphite, as the antichlor which releases no acids to attack the fibres.

Sizing.

As stated earlier in this chapter, the quality of a paper rests largely upon the manner in which sizing has been effected. After the half-stuff has been satisfactorily freed from extraneous chemicals, it undergoes mechanical treatment in water in a beating machine, where it becomes compressed into sheets and at the same time the fibres which protrude from the surfaces are removed. It is during this process that sizing operations are carried out in order that they may facilitate the matting together of the fibres to form sheets. Prior to 1807, the sizing agent used in the manufacture of papers for writing consisted of animal matter such as glue, but in that year Illig introduced rosin as a more suitable agent. To-day, rosin-sizing is generally adopted, though it should be mentioned that sizing with " water-glass " is finding favour for certain classes of paper. Rosin or colophony is the residue obtained after turpentine has been distilled off from the liquids which can be made to exude from the trunks of fir, pine, and other coniferous trees. Though it is, as may be expected, of somewhat variable composition, it is composed essentially of anhydrides of sylvic acid (abietic acid, $C_{20}H_{30}O_2$). The size is prepared by boiling the rosin for some hours with either sodium carbonate or sodium hydroxide solution, whence it dissolves to form sodium resinate, the abietic acid behaving as a monobasic acid, thus $C_{19}H_{29}COOH + NaOH \rightleftharpoons C_{19}H_{29}COONa + H_2O$. The " equivalent " of the gum can be readily found by dissolving a sample in an excess of a warm standard alcoholic solution of sodium hydroxide, and then by titrating the excess of alkali with an alcoholic solution of an acid using phenol-phthalein. Öman (*Papier-Fabr.*, 1926, **24**, Tech. Wiss. Teil, 410, 451) gives data which show that 100 grams of a typical rosin combined with 11·3 grams of NaOH, when titrated to cresol red, pH 8·0 ; 11·6 grams, using either phenol-phthalein pH 8·5, or thymol blue, pH 9·0 ; and 11·8 grams, with thymol-phthalein, pH 9·5. Had the rosin been pure abietic acid, it would have combined with 14·2 grams of NaOH.

The rosin size contains an excess of free rosin to an extent of from 15 to 25 per cent. If starch is not added to such a size before dilution with water, a milky liquid will be formed through the free rosin becoming colloidally dispersed. The agglomeration of rosin particles in the paper produces yellow specks. Sizes prepared

with the aid of " atomisers " may, however, contain as much as 40 to 45 per cent. of free rosin. These sizes are added to the half-stuff in the " beater " during the last half of the beating process and then by the interaction with a solution of aluminium sulphate added either previously or subsequently, liberates rosin and alumina upon the surfaces of the fibres, and so cements them together. A well-known book on Paper Technology suggests that " the order of adding the sizing agents appears in many cases to have but little influence on the final result," but goes on to say that " in many mills it is customary to add a portion of the alum to the beater before running in the diluted size." The actual sizing operations should be carried out between pH 3·9 and 5·5 (cf. Roschier, *Pappers och Trävarutidskrift*, 1927, 154), and for this reason it seems probable that the addition of a part at least of the aluminium sulphate before adding the size is beneficial, for in reacting with any alkali left in the pulp it will tend to precipitate aluminium hydroxide, and this is known to begin to take place at pH 4·0 to 4·1 (Britton, *J. Chem. Soc.*, 1925, **127**, 2120). Roschier states that sizing does not take place below pH 3·9, which is evidently partly due to the fact that aluminium hydroxide is then under normal conditions not precipitated. Moreover, the rosin in the size begins to flocculate at about pH 3·7 and to rise to the surface of the solution. The ideal condition is to get the rosin in the size into a very fine suspension, so that it can be readily and evenly deposited upon the fibres. Too much acid increases the size of these particles and therefore gives rise to an irregular and defective sizing. It should be stated here that abietic acid is insoluble in water. It would therefore be expected that the rosin would be precipitated immediately a sufficient amount of aluminium sulphate had been added to neutralise the alkali in the size, for the alkali contained in the size held some of the resin-acid in chemical combination and the portion present in excess of that amount was peptised by means of the prevailing alkaline reaction. This might be expected to occur at about pH 8. Actually, however, visible precipitation does ensue on account of the fact that the rosin passes first into a highly dispersed colloidal solution. Precipitation occurs at about pH 3·7. The transition from the disperse phase to the precipitate which occurs with decreasing pH is accompanied evidently by an increase in the size of the colloidal particles, which coagulate as soon as they have acquired the magnitude requisite to stop the Brownian movement which tended to keep them in colloidal suspension. Hence as Roschier states, the most satisfactory sizing conditions obtain at about pH 5, when the particles have become of the dimensions suitable for efficient

sizing. It will be observed that this pH lies about midway between the two extremes. Another advantage which is obtained by adding some aluminium sulphate before sizing, is that it sets up automatically a pH (about pH 4) and so prevents the precipitation of the curdy calcium resinates which are formed in alkaline solutions that would impair the sizing.

Much controversy has taken place as to the actual mechanism of rosin sizing, whether the sizing is due to aluminium resinate, or to rosin alone, or to rosin in conjunction with alumina. The fact is that both alumina and resin are deposited on the fibres, but the query arises when the condition is considered. The theory of sizing is of practical importance, for when the constitution of the material deposited on the fibre surface has once been established, it then will become an easy matter to find the optimum pH conditions for sizing. It cannot be merely a coincidence that the pH for sizing should be above pH 4 and should preferably be about pH 5. By analogy with some researches which the author has carried out on basic aluminium salts, including basic aluminium silicate (*vide infra*), it appears that such a pH range corresponds to the precipitation of basic aluminium sulphate, which may perhaps retain by means of weak chemical forces a little abietic acid. *The extreme weakness of aluminium hydroxide as a base*, as exemplified by the fact that it is precipitated at pH 4, *coupled with the very weakly acid nature of abietic acid, render it highly improbable that only very little, if any, chemical combination could take place between them, save perhaps a little which might possibly occur through the formation of a very insoluble aluminium resinate*. In a sizing process taking place above pH 4, it is unlikely that any aluminium resinate would be contained in the precipitate on account of the hydrolysing action which would then take place. If combination occurred between such a weak acid and a weak base by virtue of the insolubility of the salt produced, then that salt would be precipitated from solutions more acid than pH 4, and would undergo decomposition as soon as the pH of the mother-liquor exceeded 4 (*cf.* Britton, *J.C.S.*, 1925, **127**, 2146). Roschier's (*loc. cit.*) contention that basic aluminium resinate is produced at pH's below 4·5 appears therefore to be probable, but it is improbable that aluminium resinate, $Al(C_{20}H_{29}O_2)_3$, is formed at pH 5, and for that reason should give rise to best sizing. That this should be the pH requisite for efficient sizing is probably due to the fact that aluminium hydroxide then attains enhanced insolubility and therefore becomes more firmly fixed to the fibres. The following equation probably expresses the reaction which takes place in sizing :—

$$Al_2(SO_4)_3 + (6 - x)NaC_{20}H_{29}O_2 + (6 - x)H_2O$$
$$\rightarrow 2Al(OH)_{3 - \frac{x}{2}}(SO_4)_{\frac{x}{4}} \downarrow + \tfrac{1}{2}(6 - x)Na_2SO_4 + (6 - x)C_{20}H_{3\upsilon}O_2 \downarrow$$

Basic Aluminium   Free Resin.
Sulphate.
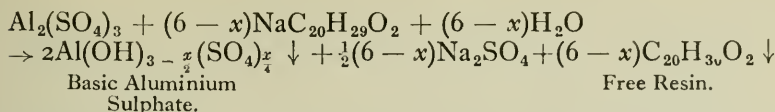
The actual value of x will depend upon the concentrations, the method of mixing, and the temperature employed. Thus, in the author's study of the precipitation of aluminium hydroxide (*J.C.S.*, 1925, **127**, 2122) 5·7 equivs. NaOH were required for complete precipitation, *i.e.*, $x = 0·3$. Whatever the true explanation may be, sulphate is always found in the sized paper, so also is resin in the free state. Roschier recommends the range pH 3·9 to 5·5 for sizing ordinary paper, and pH 5·8 for the sizing of Kraft paper, which requires the minimum amount of resin. From what has been said it seems feasible to consider sizing as being effected by the fixing to the pulp fibres of highly basic aluminium sulphate, free rosin, and perhaps a little basic aluminium resinate. Several attempts have been made to prove that aluminium resinate is precipitated by the interaction of sodium resinate and aluminium sulphate, very often by estimating the ash-contents of the dried precipitates ; but such experiments are undoubtedly vitiated by the fact that the pH's which prevail are those requisite for the separation of basic aluminium sulphate and free resin individually, and that simultaneous precipitation of alumina and rosin must occur. Resin, precipitated by acid or obtained from alcoholic solution, is said to have comparatively little sizing power, yet if alum is added after the alcoholic resin has been worked into the fibrous mass very good sizing results. The scope of this chapter does not permit of a full discussion of the theory of sizing ; the reader is, however, referred to the numerous papers by Öman in the *Papier-Fabrikant* (*Tech.-Wiss. Teil*), 1926-27.

Water-Glass Sizing.

The excellent monograph by Blasweiler (*The Use of Sodium Silicate for the Sizing of Paper ;* Constable, 1926) shows the possibilities of silica-sizing. Like rosin-sizing, it is used in conjunction with aluminium sulphate by adding to the half-beaten pulp solutions of sodium silicate, which contain for each mol. Na_2O from 2 to 4 mols. SiO_2. Sizing is often assisted by using starch, and it is essential to work the sodium silicate well into the half-stuff before the aluminium sulphate is added. The curves given in Fig. 91 refer to some work of the author on the reactions of silicic acid (*Jour. Chem. Soc.*, 1927, 425). One illustrates the pH changes undergone when a sodium silicate solution

is treated with hydrochloric acid, and shows that, although the acidic nature cannot be satisfactorily represented in terms of a dissociation constant, silicic acid has a weak, yet pronounced, acid character. Though silicic acid is quite insoluble in water, like abietic acid, it is not immediately precipitated, but passes into a colloidal solution as soon as the alkali is completely neutralised. The second curve shows that basic aluminium silicate and sulphate
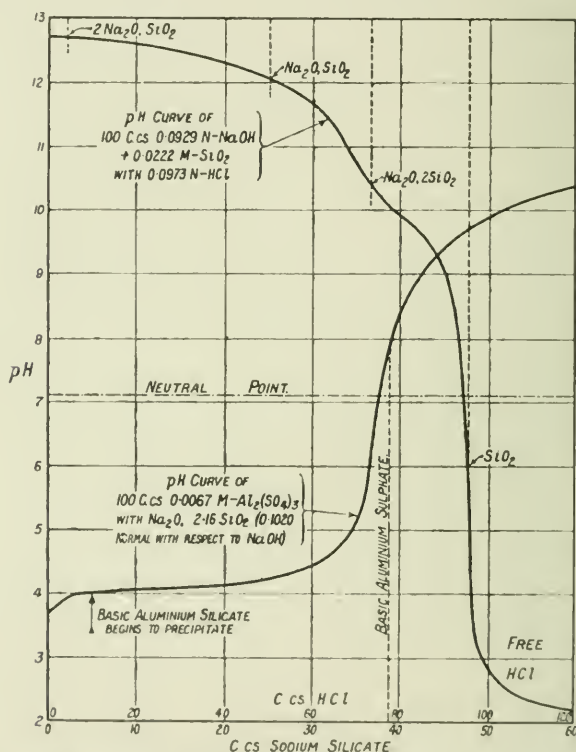
FIG. 91.—Graphs showing Acid Nature of Silicic Acid and Precipitation of Basic Aluminium Silicate.

are precipitated together at pH 4. It is exceedingly probable that a similar curve would be obtained if rosin-size were substituted for the sodium silicate. It is seen therefrom, that sizing, being essentially due to the separation of a basic colloidal precipitate within the meshes of the pulp, should be effected between pH 4 and 6, in an analogous way to rosin-sizing.

Other stages in paper manufacture which may be influenced by hydrogen-ion concentration are : (1) the introduction of filling

agents into the half-stuff, and (2) the colouring of the paper with basic and acid dyes. The amount of filling (clays, etc.) which can be satisfactorily adsorbed is dependent upon the amount of alumina deposited upon the fibres. Roschier (*loc. cit.*) finds that the best full-stuff from clay can be prepared at pH 5·0 to 5·5. Briggs and Bull (*J. Phys. Chem.*, 1922, **26,** 845) state that the taking up of dyes is a case of adsorption which varies with pH (*cf.* Speakman, *J. Soc. Dyers and Colourists*, 1925, p. 172 ; Scott, *Amer. Dyestuff's Reporter*, 1925, **14,** 862) ; and Thies (*Ind. Eng. Chem.*, 1925, **17,** 1165) claims that the maximum retention by clays of dyes is obtained at pH 4·0.

CHAPTER XXVI.

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATIONS IN BREWING.

THE hydrogen electrode was introduced into the chemistry of brewing in 1913, when Emslander (*Kolloid Zeitsch.*, 1913, **13**, 156 ; *Z. gesamte Brauwesen*, 1914, **37,** 16), a former pupil of Freundlich, used it to investigate different beers. Even at that time much information was available regarding the part played by hydrogen-ions in certain reactions which were promoted either by different enzymes, bacteria, or yeasts. Since Emslander's application of the hydrogen electrode, the concentrations of hydrogen-ions set up at the different stages in the production of beer have received, chiefly by Continental chemists, much attention. It should, however, be mentioned that beers in at least one English brewery are being examined in this way. These physico-chemical researches have led to a very real advance in our knowledge of the mechanism of brewing, though it will be understood, when the difficulties presented by such a subject are taken into consideration, that these investigations, valuable as they are, constitute but the beginning of the developments in brewing chemistry along these lines. The results so far obtained indicate how useful an index hydrogen-ion concentrations may be of the most suitable conditions for carrying out such processes as " mashing," " boiling," and " fermentation," and also of the conditions most likely to be conducive to the maximum stability of the resulting beer. Hydrogen-ion concentrations of worts and beers are, however, largely determined by the various substances originally extracted from the malt, which may exert considerable buffer action. This tends to make pH control difficult, though it seems probable that, in order to obtain more satisfactory regulation of hydrion concentrations, efforts will have to be made (a) to modify the methods of malting, (b) to modify the process of mashing, and (c) to add suitable acids or bases to the worts.

Attention will now be directed to the parts played by hydrogen-ions in the different processes involved in the brewing of beer.

Malting.

The first stage is the malting of the barley. The quality of the malt to be produced is predetermined to a great extent by the barley itself and the conditions under which it was grown and ripened. Malting comprises the artificial ripening of the corn after steeping in water, germination, and its subsequent growth until the acrospire has grown to a height equal to about three-quarters of the corn. The diastase present in reacting with the superficial starch granules renders them soluble in water, chiefly as maltose, thereby loosening the main starch-containing portion, the endosperm, and so facilitates the enzymic reactions which eventually follow in the mash tun. If the growth be forced by the use of too high a temperature, the increased diastatic action required to render food available for the growing plant will result in an unnecessary loss of starch. After growth has continued for about a fortnight, and the endosperm has acquired a mealy consistency, it is arrested, and " withered," by heaping the malt for a period of 24 hours. The malt is then dried and cured in a kiln ; the drying being effected by gradually raising the temperature while air is permitted to circulate through the kiln ; and the curing by maintaining a maximum temperature while only sufficient air is admitted for the combustion of the fires. It is during the latter stage that the flavour is developed, but great care must be exercised not to use too high a temperature, as this would seriously impair or even destroy the diastatic power. At the present time malting is carried out in an empirical way in accordance with the dictates of experience. It is certain, however, as the chemistry of brewing becomes more understood, that it will receive considerable investigation on account of the influence which the substances extractable from the malt have on the pH control which may be possible during brewing and on the ultimate stability of the beer. During malting important changes are undergone in the proteins, and it is on these, which pass into the wort, that the buffer action on the hydrogen-ion concentration depends.

Mashing.

After the malt has been suitably crushed into fine particles (not a powder), known as " grist," it is subjected to mashing, which in England takes the form of preparing an aqueous extract with warm water at about 65° C., *i.e.*, an " infusion," or when lager beer is to be produced, as is generally the case in Germany, this extraction takes the form of a " decoction," *i.e.*, after having made an initial extract by treatment with warm water, it is completed by

boiling with the malt. In the English process as much as possible of the soluble material which resisted extraction during mashing is obtained by " sparging " or spraying the malt with water at a higher temperature. The aqueous malt extract is known as " wort."

Enzymes.

From what has been written it might be imagined that mashing is merely a physical process of dissolution of the soluble portions contained in the malt. This is not the case, for the majority of substances are insoluble in water, but they are rendered soluble by the action of the *enzymes* in the malt. Enzymes are colloidal in nature, and in composition they have points in common with the proteins. So far no enzyme appears to have been isolated in the pure state, though they are known on account of the reactions which they accelerate. They are indeed catalsyts, but the catalytic activity of each enzyme or ferment seems to be selective, being restricted to the decomposition of some particular organic body or " substrate." In common with catalysts they have large surfaces compared with their masses. Each enzyme has for its maximum activity narrow limits of hydrogen-ion concentration and temperature. Van Laer (*Ann. Brass. et Dist.*, 1920, **19**, 19, 23) argues that enzymes which enable compounds to hydrolyse, *e.g.*, the inversion of cane sugar, is merely a modification of the ordinary influence which hydrogen-ions have, and that the enhanced activity is to be attributed to the high concentration of hydrogen-ions adsorbed on the surface of the enzyme. Such a concentration will be in equilibrium with the hydrogen-ions in solution, and, therefore, the maximum activity will be reflected in the pH of the solution.

We are now in a position to consider some of the reactions involved in mashing. Many are still unknown. In the first place the enzyme, diastase, in reacting with the complex starchy bodies converts them into simpler molecules of soluble starch. Now malt diastase appears to be able to do this in two different ways, by converting the starch into either dextrin or maltose. Windisch, Dietrich, and Beyer (*Wochenschrift für Brauerei*, 1923, **40**, 49, 55, 61, 67) give the optimum pH for the former reaction as pH 5·03. Ohlsson (*Comp. rend. Soc. Biol.*, 1922, **87**, 1183) explains this dual power of diastase as being due to the presence of two distinct enzymes which he calls dextrinogenase and saccharogenase, the former being destroyed at pH 4 and the latter at pH 10. The reaction which is needed in mashing is that of saccharification, and this is facili-

tated if the pH of the wort is about 4·4 to 4·5, which Sherman, Thomas, and Baldwin (*J. Amer. Chem. Soc.*, 1919, **41**, 231) have shown to be the optimum pH.   Other workers' values range from 4·6 to 5·2 (Adler, *Biochem. Z.*, 1916, **77**, 150 ; Euler and Svanberg, *Woch. Brau.*, 1921, **38**, 111).   The activity of diastase is in some way linked up with the neutral salts present, for if they are dialysed out its activity becomes diminished, but it can be regained by the addition of acids or salts, though Sherman and Thomas (*J. Amer. Chem. Soc.*, 1915, **37**, 623) found that the maximum activity can only be obtained between pH 4·2 and 4·6.

Another group of enzymes which play a very important rôle during mashing is the " phosphatases."   They act extracellularly and liberate soluble inorganic or organic phosphates.   Of the phosphates brought into solution Adler (*Biochem. Z.*, 1915, **70**, 1) found that as much as 93 per cent. was inorganic.   He states that they are active at temperatures between 42° and 60° C., with maximum activity at 58° C., the pH being 5·4.   The phosphate-content of wort is chiefly composed of a mixture of the primary and secondary acid phosphates of potassium, and the equilibria thus established exert a powerful buffer action corresponding to the second stage of the neutralisation of phosphoric acid from pH 6·0 to 7·6 (page 146).   One of the phosphatases which are involved in the mashing reactions is phytase, which accelerates the hydrolysis, optimum pH 5·2 at 48° C., of phytin, the phosphoric acid ester of the cyclic hexahydric alcohol, inositol, to liberate phosphoric acid.   Inorganic phosphates depress its hydrolysis and almost completely inhibit it at 0·009 M. at pH 5·2 (Lüers and Silbereisen, *Woch. Brau.*, 1927, **44**, 263, 273).

During mashing much of the protein matter present in the malt undergoes hydrolysis (proteolysis) under the influence of malt proteolytic enzymes, of which peptase and tryptase are the more important.   The following scheme, according to Schjerning, may be considered to show the course taken by plant proteins in passing from the insoluble condition with progressive hydrolysis through the colloidal stage to the comparatively simple soluble amino-acids :—

Insoluble Protein $\rightarrow$ Albumin II (Edestin) $\rightarrow$ Albumin I (Leucosin) $\rightarrow$ Peptones $\rightarrow$ Amino-Acids $\rightarrow$ Ammonia

Soluble albuminoids
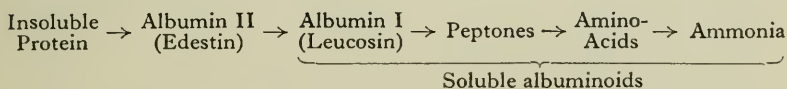
The passage of protein-decomposition products into the wort supply further buffer action, and thereby restricts hydrogen-ion concentration control.   Dufour (*Petit Jour. du Brasseur*, 1925, **33**, 1291) states that about 80 per cent. of the total buffer substances

are extracted during the preliminary stages of mashing, though an increase in buffers is found to result from " sparging." It is for this reason that a greater command over the concentrations of the buffer substances which will eventually become extracted can be procured only by altering the malting procedures. The pH most favourable for the hydrolysis of polypeptides obtained from malt proteins occurs at 4·4 to 4·5, but the temperature required is just above 40° C., which happens to be unfavourable to diastase (Lundin, *Biochem. Z.*, 1922, **131,** 193). Peptase, whose optimum pH lies between 3·7 and 4·3 in the case of kilned malt, and at 3·2 for green malt, converts leucosin into albumoses, peptones and denuclein, whereas tryptase, which brings about continued hydrolysis to amino-acids and ammonia, gives its maximum activity at pH 6·2 to 6·4. Parsons (*Jour. Inst. Brew.*, 1924, **30,** 30) gives pH 5·4 as typical of worts prepared by the English infusion process of mild ale, and 5·0 as the pH of a wort of bottling stout. As will be shown later, the existence of nitrogenous matter in beer wort is of fundamental importance in that it supplies nutrients for the yeast, and also colloidal particles of such fine dimensions as to assist in " head retention." On the contrary, protein matter, not sufficiently hydrolysed to give substances which pass into true solution, may give clear beers, though they contain colloidally-dispersed particles which on standing coagulate to form " haze." Sudden changes in temperature may also result in the formation of " haze." Moreover, the stability of the beer is to a great extent a question of nitrogen-content in that in supplying nutriment to any yeast or bacteria which it may contain will tend to set up fermentation and putrefaction.

Fig. 92 gives an electrometric titration curve, obtained by Hagues (*Jour. Inst. Brew.*, 1927, **33,** 262) with the hydrogen electrode, of 100 c.c. of beer wort with N-sodium hydroxide and N-hydrochloric acid. By comparing this curve with the one marked " water," which represents the changes in pH, when N-acid and alkali are in turn added to 100 c.c. of distilled water, the buffer action of the phosphates and organic bases present in the wort will become apparent. This unboiled wort, which may be taken as representative of worts in general, had a pH of 5·2. On adding alkali, the hydrogen-ion concentration, instead of suddenly becoming very small, as in the case of water, suffered a relatively small diminution, as shown by the very small pH change. This particular buffer action over the pH range 6 to 7·6 is largely due to the phosphoric acid in the wort being subjected to the second stage of neutralisation. The buffer action set up on adding acid is due to the presence of basic nitrogen groups, *e.g.*, $- NH_2$, in the pro-

tein decomposition products. It is noteworthy that the buffer substances in the wort are such as to produce no pronounced inflexion. This is evidently due to the presence of weak bases, and moderately weak acids, whose neutralisation curves coalesce. For further information concerning such a possibility, the reader is referred to Chapter X.

It will be seen that pH 4·4, which may be indicated by methyl orange, corresponds to that degree of acidity which promotes the maximum acitivity of the malt enzymes. Hence it might be considered that this is the pH that should be aimed at in mashing. The aim of mashing, however, is to produce a wort which contains the maximum amount of fermentable matter, $e.g.$, sugars, together
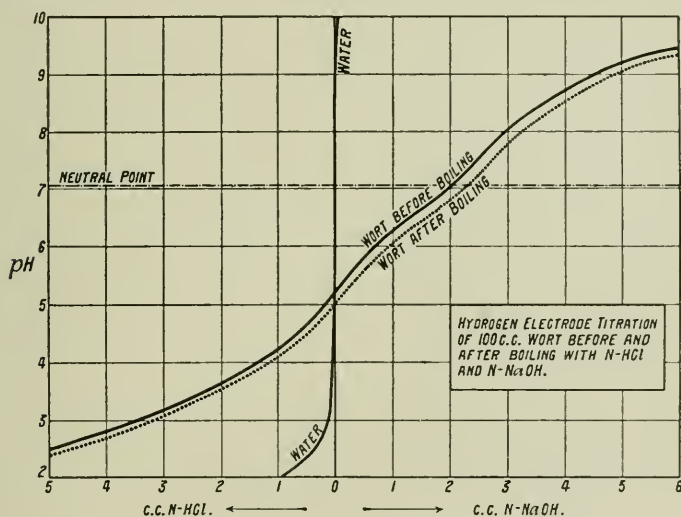
FIG. 92.—Curves showing the Buffer Action of Wort.

with an adequate amount of nitrogenous material for use in the subsequent fermentation. Although the optimum pH for the conversion of malt starch into soluble products with the aid of diastase is at pH 4·4, it happens that at such a low pH saccharification becomes difficult, so much so that it becomes completely inhibited when the pH is slightly lowered. As far as the author has been able to ascertain, the most suitable range for wort production lies between pH 5·0 and 5·5.

Varying small proportions of substitutes for malt are introduced into the wort either by the action of enzymes or by simple solution. Of the former may be mentioned corn, unmalted barley, rice, rolled maize and of the latter, various sugars such as

cane sugar, invert sugar and glucose. The glucose is usually
manufactured from sago, maize and rice starches under the in-
fluence of sulphuric acid, due regard being paid to hydrogen-ion
concentration.

Boiling.

The next stage of the manufacture of beer is one of boiling,
during which process the requisite quantity of hops is added to the
wort, and the wort becomes sterilised and concentrated.   Boiling
destroys the enzymes, causes some little caramelisation of the
sugars and assists in the extraction of the resins from the hops.
Another important point is that it causes some of the albuminoids,
which were in the wort in a condition of unstable colloidal suspen-
sion, to coagulate.   The production of caramel required for dark
beers is accomplished more easily in alkaline solution.   The partial
coagulation of the proteins is known technically as the " break."
In it hydrogen-ion concentration undoubtedly is an important
factor.   Lüers (Z. ges. Brauw., 1920, 43, 51) states that the best
" break " is obtained at pH 5·2 (cf. Hopkins, Jour. Inst. Brew.,
1921, 27, 401, and Hagues, ibid., 1927, 33, 262).   There is a
tendency for the coagulum to become less in quantity with in-
creasing acidity, perhaps through salt formation with the col-
loidal protein matter, or in the case of prolonged boiling to
partial hydrolysis of the proteins.   Hagues (loc. cit.) found
that at pH's higher than 5·0 the size of the particles of the
coagulum is the same and appears to be independent of pH ;   on
the acid side the size rapidly diminishes with increase in acidity.
The pH at which particle-size suddenly becomes sensitive to
hydrion concentration, though not sharply defined, lies, according
to Hagues, in the region of pH 5·0 or 5·1.   The fact that only
6 per cent. of the nitrogen-content of wort is coagulable on boiling
gives some idea of the proportion of protein colloidally dispersed
in the wort.   It is often said that some of the coagulum re-dis-
solves on continued boiling, some of which may probably be
precipitated from the finished beer on ageing.   Some of this re-
solution may be due to hydrolysis of the protein particles into small
particles which tend to approximate in size to molecules in true
solution.   It seems more than a coincidence that the condition
most suitable for " breaking " should be at pH 5·0, for it will be
recalled that this is not far removed from the iso-electric point,
viz., pH 4·7, of many proteins at which they possess their minimum
solubility.

    Another point which undoubtedly has some effect on the

" break " is the reaction which ensues between the tannic acid liberated from the hops and the proteins.

Boiling is generally accompanied by a slight increase in acidity. This will be seen from the lower curve, in Fig. 92, which illustrates Hague's titration of a boiled wort. The wort is then cooled in refrigerators.

Fermentation.

The boiled wort is now subjected to the fermentative action of yeast for periods of usually a week's duration at temperatures increasing from 15° to 20° C. This process may give rise not only to the formation of alcohol but of small amounts of glycerol, fusel oil, succinic, acetic, formic, and other acids. Various aldehydes and esters have been detected.

The complex nature of yeast leads to many and varied reactions. Perhaps the more important enzymes in yeast are invertase, maltase, and zymase. The function of the first two is to convert disaccharoses, *e.g.*, sucrose, maltose, into monosaccharoses, such as dextrose, and the zymase converts these monosaccharoses into alcohol. Among the factors which contribute to the activity of yeast are (1) the nutrients present in the wort, *e.g.*, nitrogenous products, which have undergone sufficient hydrolysis to form molecules of such magnitude as to enable them to diffuse through the cell walls, (2) phosphates, and (3) the hydrogen-ion concentration. Harden and Young (*Proc. Roy. Soc.*, B., 1908, **80**, 299) observed that when a phosphate was added to a fermenting mixture of dextrose and yeast juice there occurred an increase in the rate at which fermentation proceeded, and moreover, an increase in the amount of fermentation. They concluded that phosphate was probably necessary for the action of yeast, and postulated that the following equation might express the main reaction involved in alcoholic fermentation :—

$$2C_6H_{12}O_6 + 2K_2HPO_4 \rightarrow 2CO_2 + 2C_2H_5OH \\ + C_6H_{10}O_4(PO_4K_2)_2 + 2H_2O$$
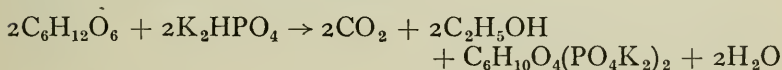
(see however Kluyver and Struyk, *Proc. K. Akad. Wetensch.*, Amsterdam, 1926, **29,** 322).

The hexose-diphosphate was believed eventually to hydrolyse back to dextrose, which according to Euler and Nordlund (*Z. physiol. Chem.*, 1921, **116,** 229) is the slower reaction, and therefore determines the rate of fermentation. They consider that a co-enzyme is necessary. Euler and Tholin (*Z. physiol. Chem.*, 1916, **97,** 269), working with dried and living yeast,

found that K_2HPO_4 accelerated fermentation, as indicated by the evolution of carbon dioxide, to a great extent at pH 4·5, but at pH 8 it retarded the gas liberation. The action of invertase in fresh yeast in presence of K_2HPO_4 on cane sugar attains a maximum at pH 4·5, and the activity of maltase of living yeast is prevented at pH 8 (Euler and Emberg, *Z. Biol.*, 1919, **69**, 349). Svanberg (*Z. tech. Biol.*, 1920, **8**, 1) finds that the optimum pH range for the growth of yeasts, whether grown in beer worts or in solutions containing ammonium salts and phosphates is for (*a*) top yeasts, pH 3 to 6, as used in worts prepared by infusion, and (*b*) bottom yeasts, pH 4 to 6, for decoction worts. Zikes (*Zentralb. Bakt.*, II., 1919, **49**, 353) finds 25° C. to be the optimum temperature. There appear to be many conditions which determine the best hydrogen-ion concentrations for fermentation. Thus Emslander (*Z. gesamte Brauwesen*, 1919, **42**, 127, 135) suggests that they should correspond to pH 4·5 for worts brewed in carbonate waters, and to pH 4·2 for worts obtained from gypseous waters ; Van Laer (*Petit. J. Brass.*, 1922, **30**, 887) considers that the presence of antiseptics, *e.g.*, hops, has some effect ; and Fodor (*Fermentforsch.*, 1920, **3**, 193), Euler and Heintze (*Arkiv. Kemi Mineralogi*, 1917, **7**, 5, 21), and Euler and Emberg (*Z. Biol.*, 1919, **69**, 349) believe that the optimum pH depends upon the colloidal nature of the different yeast enzymes, the amphoteric substrate, and particularly upon the difference in acidic nature between these colloids and their respective substrates. It is probable that these points accord with Warden's (*Amer. J. Physiol.*, 1921, **57**, 454) contention that alcoholic fermentation is the outcome of catalytic actions on the surfaces of yeast cells, and is therefore due to the considerable amount of adsorption which must take place either on the cell walls or on the colloidal particles in the yeast juice.

Regarding the optimum pH for the process of fermentation, other points are worthy of attention. It is an interesting fact that both enzymes and yeasts, when in preponderating amounts tend, through the development of certain buffer agents, to set up pH values at which they possess maximum activity. During brewing beer is very apt to be infected with bacteria and wild yeasts from the atmosphere. Among the bacteria sometimes found in beer may be mentioned *Saccharobacillus pastorianus*, which may give rise either to a bitter taste or to turbidity, *Bac. viscosus*, which may produce " ropiness," and *Bac. acetoethylicum*, which causes the formation of acetone. Hydrogen-ion concentrations may, however, be so adjusted that these bacteria and yeasts can thrive only with great difficulty, and fortunately it happens that the desirable pH, *viz.*, pH 4·5, for normal fermentation is too low

for their reproduction, though it is not entirely prevented.   Van Laer (*Comp. rend. Soc. Biol.*, 1922, **87,** 990) gives the optimum pH for the growth of the first two as pH 6·8 in hopped wort and pH 5·5 in unhopped wort, and Arzberger, Peterson, and Fred (*J. Biol. Chem.*, 1920, **44,** 465) find pH 5·8 to 6·0 for the last.

The fermentative activity of yeast alone has so far been considered, but in order for fermentation to proceed satisfactorily it is also necessary that fresh supplies of yeast be reproduced.   This the yeast does, during the fermentation of the wort, by living on the assimilable nitrogen and other nutrients which may be present. Protein-matter in the wort is rendered assimilable by the yeast by the proteolysis mainly caused by the enzymes, pepsin, tryptase, and ereptase of the yeast.   Thus yeast-pepsin converts proteins into peptones (optimum pH 4·45), which, together with polypeptides, are then with the aid of yeast-ereptase degraded into amino-acids (opimum pH 7·8), whereas yeast-tryptase hydrolyses albumin, gelatin, and casein into polypeptides and amino-acids, the optimum pH being 7.   Hence according to Dernby (*Biochem. Z.*, 1917, **81,** 109) the optimum pH for proteolysis as a whole, *i.e.*, autolysis, is 6·0 to 6·2 and the limits between which such decomposition is possible are pH 4 and 7.   The question now arises whether the wort contains enough nitrogenous matter to support the life of the yeast, and in regard to this Hulton (*Jour. Inst. Brewing*, 1922, **28,** 4) states that in worts containing the lowest amounts there is always a sufficiency.

Beer Stability.

Proteins and protein derivatives in beers exert buffer action which tend to maintain a high pH and thereby render the beers more vulnerable to the attack of wild yeasts and bacteria.   Hence the problem of beer stability has come to be associated with the nitrogenous content.   Emslander (*Z. gesamte Brauw.*, 1914, **37,** 164) holds that, the greater the amount of protein the less the stability, and Fernbach (*Ann. Brass. et Dist.*, 1923, **21,** 289) believes that yeast does not remove a sufficient amount to ensure stability. It is evident that this problem must be referred back to the malting process and the development of amino-nitrogen which occurs during the germination of the barley (Moritz and Fuller, *J. Inst. Brew.*, 1926, **32,** 602).   The reaction corresponding to stable beers, *viz.*, about pH 4, is very unfavourable to the development of the different races of *sarcina* (a most serious group of beer disease organisms) which have different optima for their growth.   The growth of some races is most rapid between pH

5·7 and 6·4 though some have an optimum at pH 5·3. It is often found that beers brewed from malts which saccharify badly, and which have fermented sluggishly, frequently have their pH well within the danger zone (Stockhausen, *Woch. Brau.*, 1925, **42**, 19, 25, 31, 37, 43 ; Stockhausen and Stege, *ibid.*, 240, 253, 261, 268). Stockhausen gives the pH range 4·0 to 4·5 for stable beers, while Parsons (*J. Inst. Brew.*, 1924, **30**, 30) regards pH 4·15 as the " safety point " for beers at " racking," beer on the acid size of this value remaining sufficiently free from bacterial activity for trade purposes.

The antiseptic power of hops is dependent on the hydrogen-ion concentration. Fernbach and Stoleru (*Ann. Brass. Dist.*, 1924, **23**, 1) found, from a study of their effect on the development of lactic acid producing organisms in *Bac. Delbruckii*, that the antiseptic activity was greatest between pH 5·5 and 6·8, had almost disappeared between pH 7·4 and 8·4, but at pH 8 the organisms were able to flourish in the hop decoction. Windisch, Kolbach, and Schüren (*Woch. Brau.*, 1925, **44**, 285, 297, 309, 324, 335, 345) have made an extended research into the antiseptic power of hops and found it to reside largely in the humulone which they contain and to be a maximum at pH 4·3, the average reaction of beer. Hence, it appears that care must be taken that the beer should have the requisite acidity, though not sufficient to become apparent to the taste, and in order to ensure the maximum preservative action of the hops, the ratio of the hop-rate to acidity must be satisfactory. Dietzel (*Kolloid-Z.*, 1926, **40**, 240) was unable to trace any parallel relationship between acid flavour and hydrogen-ion concentration.

Brewing Water Treatment.

There is no doubt that much of the quality of beer depends upon the water, and many attempts have been made to ascertain whether adjustment of the pH results in an improved wort and one containing an increased amount of malt extract. As might be expected, the different compositions of natural waters have also an important effect, and in consequence the views recorded on the question are somewhat conflicting. Perhaps one of the views having valuable practical bearing is that of Poulsen (*Woch. Brau.*, 1925, **42**, 91), who states that using calcareous water the pH of the brewing mash in a Carlsberg brewery has, since 1912, been adjusted by means of lactic acid developed in the mash by cultures of *Bac. Delbruckii.* He states that as the result of such a treatment a paler and a better flavoured beer is obtained, greater brilliancy is ensured, a better " break " having been obtained. Hagues (*J. Inst. Brew.*,

1926, **32,** 8) and Petit and Raux (*Ann. Brass. et Dist.*, 1927, **25,** 232) find that increased and better extracts are obtained by correcting the water with sulphuric acid, which on boiling give superior " breaks."

In conclusion, reference should be made to the influence which hydrogen-ion concentration may have on " head retention," " colour," and " finings." Too great an acidity produces too rapid an evolution of carbon dioxide, destroying the colloidal protein films which constitute the " head." Windisch and Kolbach (*Woch. Brau.*, 1927, **44,** 53, 64) found that the colour was affected by pH ; too high a pH tending to produce a deep colour. The efficiency of the clarification of beer by adding isinglass which on reacting with any colloidal protein matter, likely to cause " haze," brings about its coagulation, is also dependent upon hydrogen-ion concentration. It is probable that a pH somewhere near the iso-electric point of isinglass is the most satisfactory, for it is known that a beer of too great an acidity refuses to take finings.

FIG. 93.—Important pH values in Brewing.

The chart, Fig. 93, summarises the pH's of importance in brewing—it should be noted that the pH's at which various enzymes, etc., give their maximum activity have alone been indicated and not the complete pH ranges over which they are active to lesser extents.

CHAPTER XXVII.

THE SIGNIFICANCE OF THE HYDROGEN-ION CONCENTRA-
TION OF MILK.

FOA (*Compt. rend. Soc. Biol.*, 1905, **57,** 51) was the first to determine the hydrogen-ion concentration of milk by the electrometric method. Interwoven with the hydrogen-ion concentration of milk are many important properties, *viz.*, the degree of freshness and the keeping quality, the natural curdling of milk produced by bacterial action and the rate at which it takes place, the presence of blood serum, and the general composition of the milk.

pH and Titratable Acidity.

The acidity of milk is usually regarded as being either " natural " or " developed," the former being the acidity immediately after drawing from the cow, and the latter being that developed by bacterial action on standing. It may be considered in terms of titratable acidity or hydrogen-ion concentration. Titratable acidity is found by titration to phenol-phthalein with sodium hydroxide and calculated in terms of lactic acid. Actually the acidity is produced by a number of factors. Thus Rice and Markley (*Jour. Dairy Sci.*, 1924, **7,** 468) found that of the titratable acidity of freshly drawn milk, calculated as lactic acid, from 0·01 to 0·02 per cent. was due to the carbon dioxide in the milk, 0·01 per cent. to acid citrates, 0·05 to 0·08 per cent. to casein, less than 0·01 per cent. to albumin, and the remainder to phosphates. The natural acidity of milk varies between wide limits, and in extreme cases the milk drawn from individual cows may vary from 0·086 to 0·275 per cent. Usually, it varies from about 0·100 to 0·175 per cent., the average value being around 0·136 per cent. High titratable acidity of fresh milk samples may be taken as an indication of high buffer action. According to Van Slyke and Baker (*Jour. Biol. Chem.*, 1919, **40,** 342) the normal pH range of fresh milk is 6·5 to 6·65. It appears that, in a general way, a high fat content, high solids-not-fat content and high hydrogen-ion concentration of fresh milk are related. They also observed that

with diminishing hydrogen-ion concentration, there is a general tendency for the carbon dioxide to increase, whilst the titratable acidity decreases. The decrease is not so marked between pH 6·50 and 6·65, as it is above pH 6·65. The composition of milk varies with its pH value while fresh, as may be seen from the data given in Table 93, which are a selection of those given in Van Slyke and Baker's paper.

TABLE 93.

pH OF FRESH MILK AND ITS PERCENTAGE COMPOSITION.

pH.	Fat.	Casein.	Other Proteins.	Sugar.	Ash.	Chlorine.	S.G.
6·53	4·50	2·55	0·66	4·60	0·70	0·09	1·029
6·58	5·40	2·75	0·85	5·10	0·72	0·10	1·032
6·70	3·60	2·50	0·71	4·40	0·86	0·13	1·030
6·85	5·40	2·20	0·80	4·50	0·81	0·14	1·030
6·95	2·40	2·05	1·09	3·80	0·83	0·16	1 030
6·98	2·80	1·79	1·01	4·00	0·81	0·15	1·027
7·15	2·10	1·71	1·43	3·00	0·89	0·21	1·026

As these results show, there is a tendency for the specific gravity of milk to become smaller with increasing pH, and this diminution is accompanied by a reduction in the percentage amounts of total solids, fat, solds-not-fat, casein, and sugar ; and an increase in lactalbumin and proteins other than casein, and in the inorganic matter (ash) and also in the chlorine. An increase was, moreover, found to occur in the carbon dioxide content. The fact that an increased pH of fresh milk is associated with changes in the composition of the milk, including a greater carbon dioxide content, led Van Slyke and Baker to suspect that these variations were caused either by the presence of blood serum or lymph, or to an easier diffusion of the contents of blood into the milk. Despite the fact that the milk had been drawn from udders which appeared to be in a healthy condition, these variations are such as would be introduced by blood serum. Thus the pH of normal fresh milk lies between 6·5 and 6·6, that of blood serum is 7·6, and whereas the carbon dioxide content of normal milk is about 10 per cent. by volume, the content of the latter is about 65 per cent. The increase in the number of leucocytes found in milk of pH higher than 7 seemed to add support to this view, so also did the fact that fibrin was found in milks of pH 6·9 to 7·2. Conclusive evidence was, however, not forthcoming, for glucose which is a constituent of blood serum could not be detected in the milks in question. Blood serum has been found by many workers

in milk taken from diseased udders, in which case it might have found its way either by direct filtration into the lumen of the alveoli without undergoing transformation by the gland cells, or through lesions caused by bacterial activity. Baker and Breed (*Jour. Biol. Chem.*, 1920, **43**, 221) obtained similar results in that they found that milk of high pH usually contained an increased number of leucocytes and epithelial cells, and also that the percentage number of samples containing streptococci increased with the pH.

Bromocresol purple has been used by Baker and Van Slyke (*Jour. Biol. Chem.*, 1919, **40,** 357, 373) for the routine examination of milk. When 1 drop of a saturated aqueous solution is added to 3 c.c. of milk, normal fresh milk assumes a greyish-blue colour. More alkaline milks, such as those drawn from diseased udders, or which have been watered or skimmed or to which salts having alkaline reaction have been added, produce a darker colour and should consequently arouse suspicion. More acid milks, due either to developed acidity, or to having been heated above the usual temperature of pasteurisation, give rise to lighter colours. By detailed investigation of suspected samples of commercial milk they were able to detect watered milk and milk containing an excessive number of leucocytes. They also studied the rate of acid development caused through the bacteria contained in the milk by following the colour changes of the indicator after incubation in sterilised vessels for different periods of time at a given temperature. To some extent such a test gives an idea of the keeping quality, though other factors which should be considered are (*a*) the coagulation of the casein, (*b*) the development of abnormal odour and taste, (*c*) production of gas, etc. Larger numbers of bacteria were contained in the more acid samples than in the other samples. Similar observations have been made by Cooledge (Michigan Agr. Exp. Station, *Tech. Bull.*, 52, 1921) using bromothymol blue. He has also devised a test of the keeping quality by incubating at 37° C. 0·1 c.c. of milk in a tube of broth containing this indicator and making colorimetric pH measurements every hour for 8 hours.

Bacterial fermentation gives rise to that additional acidity known as " developed acidity." This form of acidity is of great importance in the manufacture of evaporated milk, for it lowers the coagulation temperature, and as a consequence, may lead to serious loss on the milk so treated. It is often found that milk with high natural acidity will not coagulate until a higher temperature is attained than that required for the coagulation of less acid milk. On the other hand, a slight increase in the developed acidity above

the natural acidity of the same milk will cause the milk to settle out at a lower temperature. Table 94, which presents the data of Rogers, Deysher, and Evans (*J. Dairy Science*, 1921, **4,** 4), gives an example of the development of titratable acidity, with lowering of pH of the raw milk, its effect on the pH of the evaporated milk and its coagulation temperature. It also gives the bacterial counts. (*See* also Holm, Deysher, and Evans, *J. Dairy Science*, 1923, **6,** 6, who obtained analogous results.)

TABLE 94.

DEVELOPMENT OF ACIDITY.

Age. Hours.	Number of Bacteria in 1 c.c. of Raw Milk.		Titratable Acidity as per Cent. Lactic Acid.	pH of Raw Milk.	pH of Evaporated Milk.	Temperature of Coagulation °C.
	Total Millions.	Lactic Millions.				
0	1·14	0·79	0·170	6·57	6·33	119
3	47·5	30·5	0·175	6·51	6·27	113
4½	96·0	53·5	0 207	6·43	6·21	110

A word here on the manufacture of evaporated and condensed milks will suffice to show the importance of the coagulation temperature, and the risk entailed in using milk with a too large developed acidity. The milk is usually subjected to a preheating treatment extending from 1 to 20 minutes at a temperature lying between 82 and 99° C., and then evaporated in vacuo between 54° and 71° C. until the desired consistency is attained. The milk is run into cans and sealed. Sterilisation of the canned milk is effected by heating to between 107° and 116° C., when every effort is made to prevent separation of the casein by efficient agitation. If coagulation has ensued, through the use of sour milk, this may often not be discovered until the can is opened by the user.

The existence of too great an acid content in condensed milk may have a deleterious effect, on account of the production of lumps of separated casein. Such an acidity may arise from a yeast which causes the fermentation of the cane sugar, or from acid-forming bacteria, or from the use in canning of an acid flux, *e.g.*, hydrochloric acid and zinc chloride. Fluxes likely to contaminate the milk, and especially those which may influence the pH of the milk should be avoided. Rosin dissolved in alcohol or in petrol is to be preferred.

Cause of Acidity.

In order to trace the cause of the acidity of milk, we must pay some attention to the composition of milk. The composition of a typical commercial sample of cow's milk is given in Table 95.

TABLE 95.

COMPOSITION OF MILK (TYPICAL).

Bases.		Acids.		Proteins.	
KOH .	. 0·038 N	H_3PO_4	. 0·063 N	Casein 28·0 gms. per litre	
NaOH .	. 0·023 N	Citric	. 0·029 N	Albumin 7·2 ,, ,,	
Ca(OH)	. 0·064 N	HCl .	. 0·028 N	Other	
$Mg(OH)_2$	. 0·016 N	H_2SO_4	. 0·003 N	Protein 0·2 ,, ,,	
	Fat . . . . . 50 gms. per litre.				
	Sugar . . . . . 47 ,, ,, ,,				

Lactic acid is not present in freshly drawn milk. It is the acid which is responsible for the developed acidity. Neither the fat nor the sugar has an effect on the hydrogen-ion concentration of milk. Hence the pH of fresh milk is determined by the reactions which take place between the several bases and the acids and amphoteric bodies (the proteins), which in a system, like that of milk, behave as acids at about pH 6·5. It is evident that at pH 6·5, the equilibria which must be involved are—

(i) $BOH + Protein \rightleftharpoons B$ Proteinate $+ H_2O$,

(ii) $BOH + BH_2PO_4 \rightleftharpoons B_2HPO_4 + H_2O$,

and   (iii) $BOH + BH_2Citrate \rightleftharpoons B_2HCitrate + H_2O$
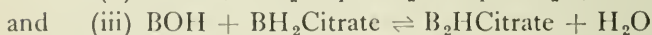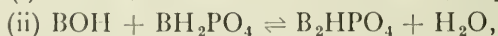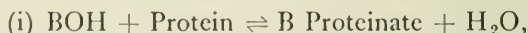
where B represents the equivalent weight of any of the strong bases given in Table 95. If we consider the data given in the table, we find that the total concentration of bases is 0·077 N, whilst the total concentration of acids which form either neutral salts or acid salts below pH 6·5, e.g., NaH_2PO_4 and NaH_2 Citrate, is 0·061 N. Hence a concentration of 0·016 N of the bases will be free to form either of the secondary salts, Na_2HPO_4 and Na_2H Citrate, and to react with the casein and other proteins. As the casein is in a preponderating amount it appears that in milk much of the excess base will combine with it. Harris (*Proc. Roy. Soc.*, 1924, **97**, B, 372) has pointed out that if separate pH-acid combination curves for each of these constituents be plotted, making the abscissæ proportional to the percentage amounts present, the re-

sultant curve obtained by summation gives a pH-acid combination curve for the whole milk, which will be found to agree excellently with the experimentally determined curve.   In general, the ash in milk bears a direct proportion to the protein in the ratio of 2 : 9, *e.g.*, Richmond (*Dairy Chemistry*, p. 152, 2nd ed., London, 1914) gives protein 37·8 per cent., and ash 8·3 per cent., of the solids-not-fat, and of this ash the phosphate and citrate contents are approximately constant.   Furthermore, the lactalbumin bears a small, but definite, ratio to the casein content.   On these grounds, Harris argues " that in moderately acid solutions the buffer value of normal cow's milk is directly proportional to the amount of protein present (as also, therefore, to the phosphate, citrate, etc.)." A pH curve of 100 c.c. of a representative sample of milk is given in Fig. 94, which is reproduced from a paper by Clark (*J. Dairy Science*, 1927, **10**, 199).

Estimation of Protein in Milk.

Based on the above statement, Harris has devised a method by which he claims that the protein in milk can be estimated within 0·1 per cent.   It is only necessary to run from a burette successive small amounts of decinormal hydrochloric acid to a measured volume of milk and to determine the pH after three or four additions.   These should be sufficient to construct a pH-acid curve, and as the curve is practically rectilinear, it is possible to interpolate the amount of
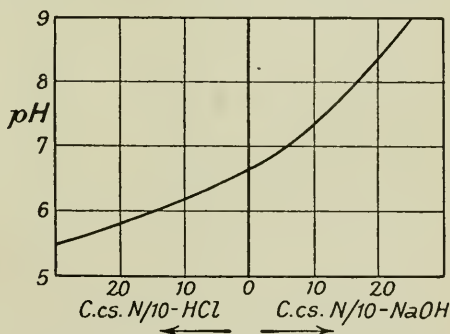
FIG. 94.—pH Curve of 100 c.c. of Milk.

N/10–HCl to be added to take the pH of the milk from one given value to another.   Such an amount of acid will be proportional to the protein content.   By choosing 10 c.c. of milk as the volume to be titrated and the pH range, 6·65 to 5·2, the amount of N/10–HCl may be taken as numerically equal to the percentage of the protein in the milk.   Harris adds that the readings should be taken only within the range, pH 6·7 to 4, the reason for which will be apparent from Fig. 94.   Clark finds the buffer capacity, $\dfrac{dB}{dp\mathrm{H}}$, *i.e.*, $= \dfrac{\text{Equivs. acid or alkali added to 1 litre}}{\text{Change in } p\mathrm{H}}$,

of the milk at pH 6·0 to be 0·0242 and 0·0186 at pH 6·6. It is interesting to compare these values with that of blood. As is well-known, human blood is well buffered and at pH 7·4 $\frac{d\mathrm{B}}{dp\mathrm{H}} =$ 0·0228. The buffering of milk has been studied recently by Buchanan and Peterson (*J. Dairy Science*, 1927, **10**, 224).

It happens that if different samples of milk had widely differing buffer capacities, a highly buffered milk would resist the action of the lactic acid, developed by means of bacteria, as regards its hydrogen-ion concentration to a greater extent than a poorly buffered sample. In the former case, considerably more lactic acid would be required to cause the milk to coagulate than in the latter. For milk to curdle the hydrogen-ion concentration is of utmost importance, so also is it in regard to the rate at which curdling takes place. Michaelis and Mendelssohn (*Biochem. Zeitsch.*, 1915, **58**, 315) found that the optimum concentration of hydrogen-ions required to precipitate casein by acids in pure solutions or in milk is $2·5 \times 10^{-5}$, and Allemann (*Biochem. Zeitsch.*, 1912, **45**, 346) obtained $1·3 \times 10^{-5}$ as the minimum concentration. Van Slyke and Baker (New York Agric. Exp. Station, Geneva, *Tech. Bull.*, **65**, 1918) coagulate the pure casein from milk at pH 4·64 to 4·78 by carefully introducing hydrochloric and lactic acids into the body of the milk and then centrifuging. The correct acidity is adjusted with bromocresol purple. Waterman (*J. Assoc. Off. Agric. Chem.*, 1927, **10**, 259) uses for the precipitation of the casein a buffer mixture which controls the pH of precipitation within a range of about 0·04 for fresh milk samples, and precipitation is effected at a pH very near to the isolectric point of casein.

As a rule, fresh milk having a high hydrogen-ion concentration has also a high titratable acidity due to the presence of a high acid phosphate and, maybe citrate, content. Such milk, despite its acidity, is of greater nutritive value than milk low in acid. The casein content of the more acid milk is higher. It is also found, as might be expected, that fresh milk of low pH undergoes a smaller variation in hydrogen-ion concentration on the addition of either acid or alkali. High acid milks are of importance commercially for this reason, for on storing they take longer time to reach the point of coagulation than low acid milk. The carbon dioxide content of milk remains fairly constant, though there is a tendency for milk of high pH to contain greater amounts.

We have seen on page 329 that calcium phosphate begins to precipitate under conditions of equilibrium at about pH 5·5, whilst at higher pH values, it becomes increasingly insoluble. It

is probably the complexity and colloidal nature of the milk system which prevent the precipitation of calcium phosphate from ordinary milk. It is, incidentally, extremely probable that both the calcium and the phosphate are much more readily assimilated from a highly acid fresh milk than from a less acid milk—a point which may have bearing on the prevention of rickets (*cf.* Clark, *J. Dairy Science*, 1927, **10,** 199).

Colorimetric Determination of the *p*H of Milk.

The absorption of the indicator by the casein in milk presents difficulty in the measurement of its hydrogen-ion concentration. Hence, various methods have been adopted in which the casein is eliminated by dialysis, or its effect minimised by dilution (*cf.* Schultz and Chandler, *J. Biol. Chem.*, 1921, **46,** 129 ; Schultz, Marx, and Beaver, *J. Dairy Sci.*, 1921, **4,** 1 ; Kramer and Greene, *J. Biol. Chem.*, 1921, **46,** 42 ; Brown, *J. Physiol.*, 1920-1, **54,** 167).

The dilution method has been carefully investigated by Sharp and McInerney (*J. Biol. Chem.*, 1926, **70,** 742). They dilute 1 part of the milk product with 19 parts of distilled water, and then perform the colorimetric determination of the *p*H value with the comparator as described on page 228. The values so found are too high. Table 96 gives the true *p*H values of both the undiluted milk and the undiluted whey corresponding to the observed values on the diluted samples. The values given in the second column also refer to whole and skim milk and to heated milk. They may be used for evaporated milk, if it first be diluted to the consistency of whole milk, and further diluted as stated above. The *p*H values of undiluted whey do not apply if a part of the casein only has been precipitated, and moreover, if satisfactory values for whey are to be obtained the determinations must be made immediately after the curd has been separated. The amount of indicator recommended is 5 drops of 0·1 per cent. solution to each 10 c.c. of solution.

Concerning the *p*H of cream, Sharp and McInerney state that fresh cream is supposed to have the same hydrogen-ion concentration as the skim milk which may be centrifuged from it. Provided the cream has not developed acidity, in which case the skim milk will contain products intermediate between curds and whey, the foregoing dilution method can be adopted and the relationships given in columns I. and II. of Table 96 will hold good. For sweetened condensed milk, they dilute the milk with distilled water back to the average solids-not-fat composition of the

TABLE 96.

RELATION BETWEEN pH OF DILUTED MILK AND OF ORIGINAL MILK.

Observed pH Diluted Product.	pH Undiluted Milk.	pH Undiluted Whey.	Indicator.
7·4	6·86	—	
7·3	6·76	—	
7·2	6·66	6·94	
7·1	6·56	6·84	
7·0	6·46	6·74	Phenol Red
6·9	6·36	6·64	
6·8	6·26	6·54	
6·7	6·16	6·44	
6·6	6·06	6·34	
6·5	5·96	6·24	
6·4	5·86	6·15	Bromo-cresol Purple
6·3	5·76	6·05	
6·2	5·66	5·96	
6·1	5·57	5·87	
6·0	5·48	5·77	
5·9	5·40	5·68	
5·8	5·32	5·58	
5·7	5·24	5·48	Chloro-phenol Red
5·6	5·17	5·38	
5·5	5·11	5·28	
5·4	5·05	5·18	
5·3	4·99	5·08	
5·2	4·92	4·98	
5·1	4·86	4·88	
5·0	4·78	4·78	
4·9	4·71	4·68	
4·8	4·62	4·58	Bromo-cresol Green
4·7	4·53	4·48	
4·6	4·44	4·38	
4·5	4·34	4·28	
4·4	4·25	4·18	
4·3	4·15	4·08	
4·2 (?)	4·05	3·98	Bromo-phenol Blue
4·1 (?)	3·94	3·88	
4·0 (?)	3·84	3·78	

uncondensed milk, and then to 20 volumes before determining the pH. The values given in Table 96 are not applicable. For a normal product so treated, 0·85 pH is subtracted from the observed value in order to arrive at the hydrogen-ion concentration of the reconstituted milk. The pH of the sweetened condensed milk is approximately 0·30 pH less than the latter value.

Relation between Titratable Acidity and pH.

The work of Sharp and McInerney (*J. Biol. Chem.*, 1927, **75**, 177) has shown that there exists between the titratable acidity of

fresh milk, if it be greater than o·1 per cent., a relation by which the pH value can be ascertained with an average error of $\pm$ o·06 pH. This relation is expressed by the heavy curve in Fig. 95. The thin lined curves show the development of acidity by the souring of samples of milk, whose acidities, when fresh, are represented by the points of intersection of these curves and the
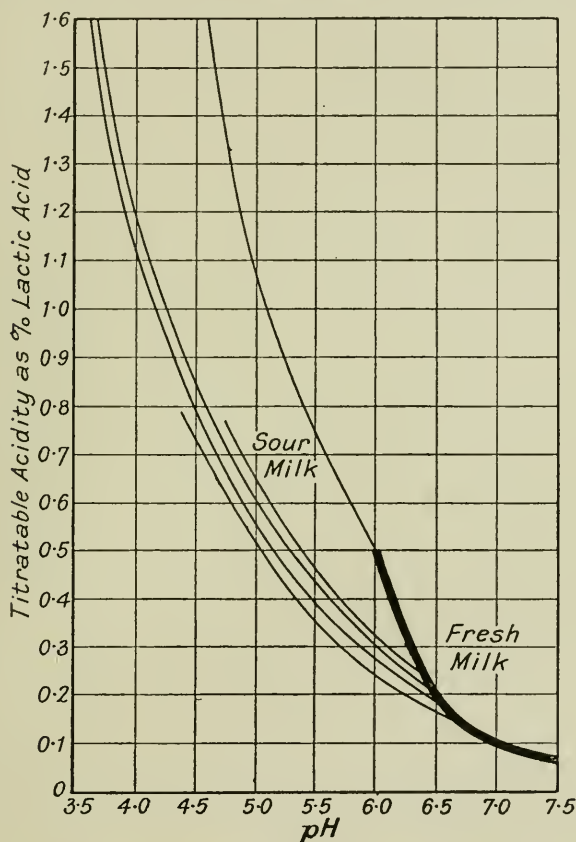
FIG. 95.—Relation between the pH of Fresh and Sour Milk.

heavy lined curve. It will be seen therefore that quite a different relationship exists between the titratable acidity of sour milk and the pH readings. From this, it follows that a knowledge of both the titratable acidity and the pH value of a milk may be of great value in ascertaining the condition of the acidity of the milk, whether it be natural or developed. Titratable acidity, by itself, is of little use in this respect. In order to make these investigations

as complete as possible Sharp and McInerney studied, as shown by Fig. 95, samples of fresh milk which ranged in titratable acidity from 0·50 per cent. to 0·05 per cent. as lactic acid and from pH 6·0 to pH 7·73. The milks corresponding to the extreme acidities were abnormal. Thus, those of abnormally high titratable acidity and high hydrogen-ion concentration were all samples of colostrum milk or milk drawn in the early days of lactation, though it should be mentioned that samples of the latter were not always of abnormal acidity. It is interesting to note that they found the milks lying at the other extreme, $viz.$, high pH, often contained large numbers of leucocytes, which in many cases were traced either to diseased udders, or to gargety milk, or to cows which had not been milked for some time. In view of these abnormalities, it is somewhat surprising that the general relationship shown by Fig. 95 should exist.

Cows' milk, on account of its appreciable buffer action and high pH, is somewhat difficult to digest by infants. It may be improved by adjusting the pH value to approximately that of human milk, $viz.$, about pH 5·5. Hess and Matner ($J. Amer. Med. Assoc.$, **82**, 1604) have found that lemon juice or orange juice can be added directly to cows' milk without curdling, and that by mixing approximately 21 c.c. of lemon juice with a quart of milk the pH value fell from 6·64 to 5·54. They state that the infants who received milk so treated, thrived. Either lactic or hydrochloric acids may be used, but lemon juice is to be preferred in that it compensates for the deficiency in cows' milk of anti-scorbutic vitamin. The addition of egg yolk to the treated milk is without any marked change on its pH value.

Another case in which the adjustment of the hydrogen-ion concentration has been put to practical use is the separation of milk-fat from sour cream (Stevenson, U.S.P. 1,397,664/1922). Hydrochloric acid is added to the diluted cream until pH 3·0 is attained, at which value the precipitated casein will have re-dissolved, so that the milk-fat may be separated centrifugally.

Hydrogen-ion concentration control in the making of Swiss cheese has been advocated by Sammis and Santschi ($J. Dairy Sci.$, 1924, **7**, 83) and by Watson ($Ind. Eng. Chem.$, 1927, **19**, 1272). The former add 1 drop of 0·01 per cent. solution of bromocresol purple to 1 c.c. of well-mixed whey, and when the acidity has developed to the extent required just to turn the indicator yellow, they proceed with the final step in the process. Watson uses the quinhydrone electrode.

CHAPTER XXVIII.

THE IMPORTANCE OF HYDROGEN-ION CONCENTRATIONS IN BAKING.

THE successful production of bread is apt to be regarded as an industry which is dependent chiefly upon the skill of the baker, and to a lesser extent upon the flour available. It might therefore be argued that the baking industry is one of the few which lies outside the possibilities of scientific control, and that the quality of the bread manufactured must necessarily be the result of trial and error. This state of affairs has undoubtedly been aggravated by the inability of the chemist to delve into the complex nature of the proteins present in flour, and of the enzymic reactions which occur during the preparation of the dough, and later on in the first stages of baking. Though, perhaps, the recent advances made in this special branch of chemistry may not be considered as epoch-making, one thing is certain, that the correlation of the changes in hydrogen-ion concentration during the combination of the proteins with acids and bases together with the variations in their physical properties, provides in hydrogen-ion concentration measurements an effective means of controlling baking processes. It is, moreover, a fact that some efforts are now being made to control baking processes on the industrial scale in such a way. Such control applies particularly to the times required for efficient fermentation of the dough before moulding and placing in the oven. It is, of course, futile to prophecy that bakers will adopt these methods in their daily routine, but it is evident that millers are endeavouring to provide, and bakers to use, flours which have been improved as far as their baking properties are concerned by the inclusion of some harmless ingredient, whose initial effect is generally found to raise the hydrogen-ion concentration of the aqueous extract of the flour. Additional improving treatment is very often accorded by the bakers themselves. Such an " improver " is acid calcium phosphate, a variable mixture of mono- and dicalcium phosphate. Formerly alum was employed for this purpose, and as was pointed out by Jessen-Hansen, its efficacy was undoubtedly

due to the appreciable amount of acid which it hydrolyses and thereby enables a better loaf to be produced.

In order to make clear that which follows relating to the rôle played by hydrogen-ions in different concentrations some attention will now be directed to flour. Wheat flour comprises colloidal bodies, chiefly starch and proteins, water, and a very small amount of crystalloidal bodies, namely, sugars and mineral matter. According to Kent-Jones (*Modern Cereal Chemistry*, Liverpool, 1927), the different flours and wheats show relatively little variation in their analyses, as shown in Table 97.

Table 97.

Composition of Wheat and Flour.

	Wheat.	Flour.
	Per Cent.	Per Cent.
Starch	$63–71$	$65–70$
Proteins	$10–15$	$9–14$
Water	$8–17$	$13–15$
Cellulose	$2–3$	}
Fat	$1\frac{1}{2}–2$	} 1
Sugars	$2\frac{1}{4}–3\frac{1}{2}$	$2\frac{1}{2}$
Mineral Matter (ash) . . .	$1\frac{1}{2}–2$	$\frac{1}{2}$

The mineral matter as ash constitutes from 0·3 to 0·7 per cent. of the flour, and, as the following typical analytical figures show, is made up of phosphoric acid partially neutralised by potash, magnesia, and lime : K_2O 37·04 per cent., MgO 6·12 per cent., CaO 5·53 per cent., Fe_2O_3 and Al_2O_3 0·36 per cent., P_2O_5 49·11 per cent., SO_3 0·40 per cent. (Kent-Jones). Despite the fact that analyses of flours show only slight variations, flours differ widely in their baking properties, which have been traced mainly to the colloidal properties of the proteins, and also to the changes in these properties which occur by varying the hydrogen-ion concentrations. Flours have become to be known as either " strong " or " weak " according as to whether they bake well or badly. Thus Humphries and Biffen (*Jour. Agric. Sci.*, 1907, **1**, 1) defined a " strong wheat " as being one " which yields flour capable of making large, well-piled loaves." Such a definition is vague, and should include the condition of giving a satisfactory texture. Moreover, the formation of well-piled loaves may be due merely to an inadequacy of diastatic action to produce the necessary sugars for the maintenance of the activity of the

yeast.   Sharp and Gortner (*J. Physical Chem.*, 1922, **26**, 101) suggest that there are " at least three classes of weak flour," having, either

(1) Weakness due to the inferior quality of the gluten, though present in an adequate quantity,

(2) Weakness due to an inadequate quantity of good gluten ; or

(3) Weakness due to factors influencing yeast activity.

Much of the starch present in flour appears to resist decomposition during baking on account of the difficulty in rupturing the cellulose coverings of the starch granules.   The ease with which the starch contents of the various flours may thereby become available to diastatic decomposition, provides in the opinion of Collatz (*Amer. Inst. Baking*, 1922, *Bull.* No. 9), an important point of difference between strong and weak flours, for the greater amount of sugars formed in strong flours permits of a plentiful supply of carbon dioxide being developed during fermentation, which is necessary to raise the dough.

The production of well-piled loaves necessitates the formation of dough of such a fine texture as not to be readily pervious to gas ; in other words, to have a good gas-retaining property, and moreover, to be able to retain it during the early stages of baking in the oven.   This property is intimately connected with the proteins of the flour.   The chief proteins are *gliadin* and *glutenin*, the latter imparting solidity, whereas the former is soft and sticky and consequently adheres to the glutenin to form a coherent mass.   On adding water to flour, hydration ensues with the formation of a colloidal complex, *gluten*, from these proteins.   There is very little difference in the percentage compositions of gliadin and glutenin, but the differences occur in their physical properties. Gliadin can be extracted by means of 70 per cent. alcohol.   The gas retention of doughs then depends upon the dispersion, coherence, elasticity and the imbibition water content of the gluten, and these factors have been found to be influenced by acids and salts in various concentrations.   In order that gliadin, which according to Lüers (*Kolloid Z.*, 1919, **25**, 177, 230) is the more important protein, may yield the best baking results, a certain degree of swelling must be attained, and this can be produced if due regard be paid to such factors as hydrogen-ion concentration, electrolytes, temperature, and time.

Two objects have to be kept in view in the milling of flour, namely (*a*) to obtain the maximum yield of flour from the wheat— about 10 per cent. is generally lost—and (*b*) to produce a flour

having the most satisfactory baking properties. Various treatments may be resorted to in the conditioning of the wheat, such as drying in the case of damp wheats, adding water, subjection to a suitable temperature for a certain length of time, and finally grinding. Conditioning, though originally introduced in order to toughen the bran to prevent pulverising it during grinding, so as to effect a better separation from the endosperm, may have an important effect upon the colloidal properties of the flour proteins and thereby influence the baking strength of the flour. Tague (*J. Agric. Research*, 1920, **20,** 271) has investigated the changes involved during the tempering of wheat by measuring the *p*H, titratable acidity, titratable nitrogen by the Sørensen Formol method and of the amount of water-soluble phosphorus. He concluded that the changes undergone in producing wheat of good milling quality were physical in character and occurred after maintaining the wheat at 20° to 25° C. for 48 hours so that it had a moisture-content of $15\frac{1}{2}$ per cent. Increase in temperature gave increased hydrogen-ion concentration, titratable acidity, nitrogen and a greater quantity of water-soluble phosphorus. A temperature of 5° C. gave a wheat of higher *p*H, but one which was brittle and hard, whereas 40° C. gave a sticky product. Kent-Jones (*Modern Cereal Chemistry*, 1927, p. 294) states, however, that " experience has shown that the best course is to differentiate entirely between any strengthening process and any conditioning process," and that the latter operation " should be restricted to getting the wheat into as nice a milling state as possible, and no attempt should be made to perform the heat-treatment in the same operation." As the processes involved in milling bring about a change in the physical state of the flour, it could hardly be expected that *p*H determinations could provide any means of control—and this is in agreement with the experience of Weaver (*Cereal Chem.*, 1925, **2,** 209).

*p*H of Flour Extracts.

The hydrogen-ion concentration of flours is largely determined by the protein substances and phosphates which pass into the aqueous extract. These behave as very efficient buffers and usually maintain a hydrion-concentration of a little above *p*H 6. The *p*H's of water extracts of flours were investigated by Bailey and Peterson (*Ind. Eng. Chem.*, 1921, **13,** 916), who found that the time allowed for the extraction and the temperature at which it was carried out had scarcely any effect upon the *p*H. Their extracts were made by treating 1 part of flour with 5 parts of water. This will be seen from the results given in Table 98, which are typical data.

TABLE 98.

EFFECT OF TEMPERATURE ON THE pH OF FLOUR EXTRACTS.

Temperature.				Flour.	pH of Extract.	Flour.	pH of Extract.
0° C.	.	.	.	Patent	6·10–6·09	Clear	6·29–6·27
25° C.	.	.	.	,,	6·05–6·05	,,	6·30–6·31
40° C.	.	.	.	,,	6·00–5·99	,,	6·29–6·30
60° C.	.	.	.	,,	6·04–6·04	,,	6·25–6·25

The ranges of pH correspond to extracts prepared by allowing 1, 2, 4, and 6 hours. Furthermore, Kent-Jones (*loc. cit.*) has shown that it is immaterial what proportion of flour is used in preparing the extract, and also whether the pH determination is made on the filtered extract or on the flour suspension itself. These hydrogen-ion concentrations should provide some valuable indication of the baking strengths of the flours, for they represent equilibrium conditions of the reactions which are set up between the flours and the aqueous extracts. These equilibria can only be established at the flour-water interface, and they in turn determine the degree of dispersion and viscosity of the suspensions—both factors being of importance in the production of a satisfactory dough. It is in facilitating the rapid attainment of equilibrium between flour particles and water that (*a*) the problem of efficient grinding to give them a large surface, and (*b*) the moisture contents become of great importance. It is not surprising therefore that the better quality flours, *i.e.*, better as regards baking strength, impart to the aqueous extracts greater hydrogen-ion concentrations than do the poorer quality flours. Thus Bailey and Peterson's data (*loc. cit.*) given in Table 99 show that the better

TABLE 99.

pH AND QUALITY OF FLOUR.

Grade of Flour.		pH.	Per Cent. Ash.	Grade of Flour.		pH.	Per Cent. Ash.
Patent	.	6·02	0·40	3rd Break	.	6·22	0·67
1st Middlings	.	6·07	0·44	1st Clear	.	6·40	0·83
2nd Middlings	.	6·10	0·45	4th Middlings	.	6·42	1·17
3rd Middlings	.	6·22	0·55	1st Break	.	6·24	1·34
2nd Break	.	6·25	0·58	2nd Break	.	6·44	2·38
5th Middlings	.	6·31	0·61				

grades of flour give the lower pH. They possess incidentally, as shown, the lower ash contents, and as the inorganic constituents of flour comprise soluble phosphates, it is reasonable to imagine that the smaller the ash-content the smaller will be the buffer action on the hydrogen-ion concentration of the flour extract. This may explain the lower pH of the better grades of flour as shown in the above table. Similar data were obtained by Kent-Jones (*loc. cit.*) for flours produced in England which are as follow : Commercial Patent, pH 5·90 ; English (straight run), pH 6·28 ; Commercial Bakers' (straight run), pH 6·20 ; and Low Grade Commercial pH 6·50.

Buffer Action of Flours.

The ease with which the pH of a flour can be lowered by the acid developed during the fermentation process is one factor on which the efficiency of that process depends. This is the same
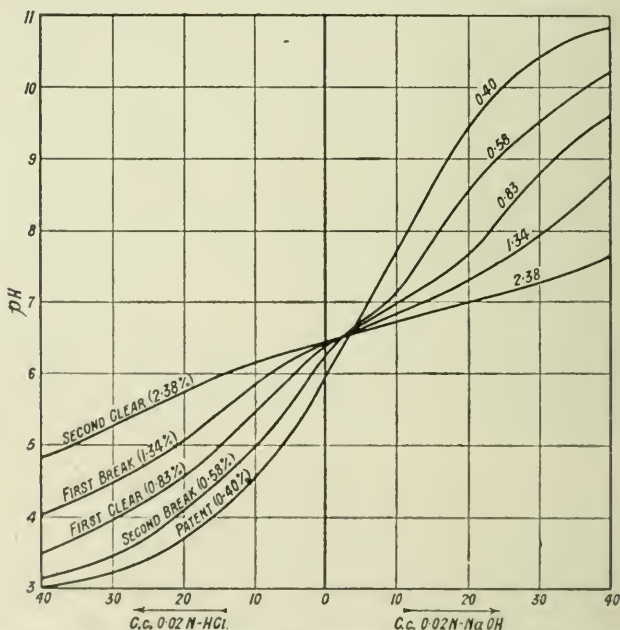
Fig. 96.—Hydrogen Electrode Titration Curves of Flour Extracts.

as saying that the proportion of buffers present in a flour should be small. Fig. 96 gives typical electrometric titration curves, using the hydrogen electrode, of 100 c.c. of aqueous extracts of different grades of flours with 0·02 N-HCl and 0·02 N-NaOH. They are

taken from Bailey and Peterson's paper, and refer to the flours given in Table 99. The numbers enclosed in brackets are the percentage ash-contents. It will be observed that the best grade— Patent—having the lowest ash, 0·40 per cent., gave rise to the greatest change in pH when either hydrochloric acid or sodium hydroxide was added, and that these effects became less with the increasing content of mineral matter. As mentioned previously much of the mineral matter comprises acid phosphates. The second dissociation constant of phosphoric acid is $1·4 \times 10^{-7}$, and therefore the pH corresponding to half-neutralisation of the second stage will be equal to $p\mathrm{K}_2$, *i.e.*, 6·85. This will be the pH at which the maximum buffer action will be exerted, so that if much phosphoric acid be present small additions of either acid or alkali will cause comparatively small pH changes (compare phosphoric acid curve on page 398). These remarks explain both the positions and the shapes of Bailey and Peterson's curves. Kent-Jones records the buffer action of flours by taking the pH of a water extract, then again after 10 c.c. 0·01 N-lactic acid has been added to 100 c.c. of extract, and multiplying the diminution in pH by 10.

pH and Fermentation.

Flour contains a certain amount of diastase produced during germination of the wheat, which during the dough preparation brings about the conversion of the available starch into maltose, which in turn through the enzyme, maltase, passes into dextrose. This is particularly the case when either malt-extract or malt-flour is added in order to supplement, when necessary, the diastatic activity. An adequate supply of these sugars, dextrose and maltose, in the dough is required to support the activity of the zymase in the added yeast. Zymase breaks down the sugar to form carbon dioxide and ethyl alcohol, so that the dough becomes aerated and raised by the gas and alcohol vapour. Rumsey (*Amer. Inst. Baking*, 1922, *Bull*. No. 8) has investigated the influence of hydrogen-ion concentration on the activity of wheat flour diastase. His data, plotted in Fig. 97, show the relationship between the amounts of maltose formed when 10 grams of a flour, after having been brought to the desired pH by the addition of acid or alkali, were digested at 27° C. for one hour, and the pH then attained. The maximum activity occurred at a pH between 4·7 and 4·8, with a broader range between pH 4·0 and 5·3. This optimum pH, 4·7 to 5·0, is also that found by Sherman, Thomas, and Baldwin (*J. Amer. Chem. Soc.*, 1919, **41,** 231) for the activity of the diastase of malted barley.

It should be stated that the temperature 27° C. was chosen because it is that at which fermentation is effected. Increased activity occurs with longer time, but at this temperature the increase after 60 minutes' digestion is uniform and gradual. With higher temperatures the increase in maltose formation becomes much more rapid. Working with one-hour digestions at different temperatures it was found that the greatest activity occurred at 63·5° C. Collatz (*Amer. Inst. Baking*, 1922, *Bull*. No. 9) made similar observations with malt flour and found that the optimum pH for the amylase contained therein was pH 4·26, though the activity
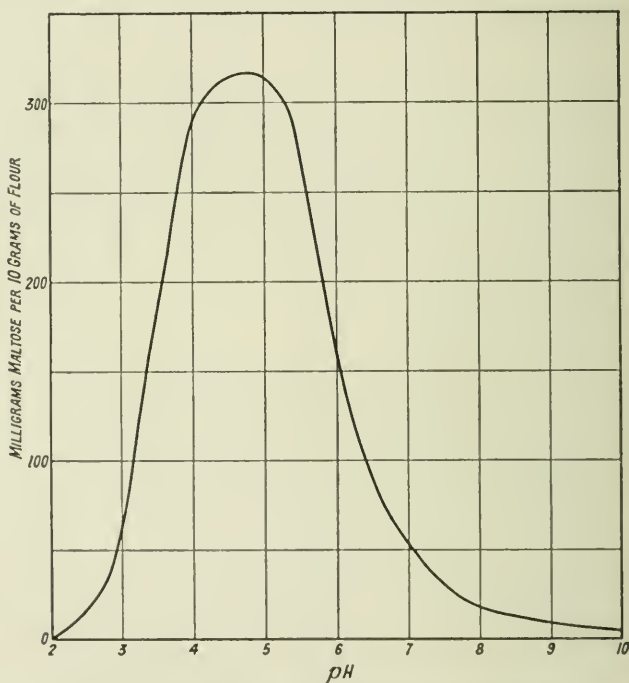
Fig. 97.—pH and Activity of Wheat Flour Diastase.

was still considerable between pH 3·5 and 5·5. Care must be exercised in the use of malt extract to employ just that quantity which will give the requisite amount of diastatic activity. Should it be excessive the dough becomes sticky and runs, and on baking may yield a loaf sticky in the centre, or the dough may even fail to bake.

Hydrion concentrations play an important part in the fermenting stage. Thus the maximum rate of fermentation is reached at pH 5·0, and also the proteolytic enzymes in the yeast act

best in the neighbourhood of pH 5·0. Though much of the gas-retaining power of the dough is inherent in the quality of the gluten, which is influenced by both the quality and quantity of its glutenin, much will depend upon any further change in the dough brought about through the action of protease ; if this has not been too great it may have a beneficial effect in softening the dough. Another reason why doughing should be carried out at a pH near to 5 is that the isolectric point of flour proteins is situated in its vicinity, and this accounts for the fact that it is here that the dough is generally most coherent and elastic.

The variations in hydrogen-ion concentration during the fermenting of doughs have been studied by Bailey and Sherwood (*Ind. Eng. Chem.*, 1923, **15,** 624) with very interesting results. They found that the hydrion concentration increases at a fairly uniform rate in bread doughs fermented under fixed conditions, and increasing the temperature, as in " proving," when the dough is finally moulded and placed in the oven, accelerates the rate of increase. This increase in true acidity is due to the production of organic acids by the various yeast enzymes. " Sponge doughs," in contrast with the ordinary " straight doughs," are made with a greater proportion of water by mixing with it at first a portion only of the flour, and then incorporating the remaining quantity of flour after fermentation has proceeded for a fairly long period. These doughs undergo a more rapid increase in the concentration of hydrogen-ions. The rate of increase in hydrion concentration appears to depend upon (*a*) the grade of flour, the doughs formed from high-grade or patent doughs changing more rapidly in pH than do those prepared from low-grade or clear flours, and (*b*) the consistency of the dough. Table 100 gives the change in pH found by Bailey and Sherwood.

TABLE 100.
pH OF FERMENTING DOUGHS.

Time of Fermentation (Minutes).	Patent. pH.	Clear. pH.	I pH.	II pH.	With Acid Phosphates and Malt Extract.	
					I pH.	II pH.
0	5·59	5·85	5·43	5·64	5·36	5·54
120	5·44	5·65	5·22	5·38	4·99	5·28
240	5·20	5·48	5·01	5·20	4·73	5·01
360	4·83	5·27	4·89	5·04	4·70	4·85

It will be observed that the dough made from clear, low-grade flour, owing to its great buffer content, did not undergo change in pH as quickly as did the patent flour dough. Yet it is found by practical

experience that low grades cannot be subjected to fermentation for as long as the better grades, and therefore they cannot acquire that pH which permits of maximum yeast activity. Thus, in the case of the patent and clear doughs Bailey and Sherwood state that patent doughs are ready for moulding in about 270 minutes, whereas the time for clear doughs is 225 minutes. Hence, to see if doughs could be made to acquire a higher concentration of hydrogen-ions, they added to doughs I and II a mixture of acid phosphates, phosphoric acid and malt extract, and obtained more acid doughs (see Table 100) which were ready for moulding in 300 minutes and which led also to an improvement in colour, grain and texture of the resulting loaves. Moreover, with such a pH the yeast activity was so enhanced that the volume of yeast used could be reduced without impairing the bread. Their data corresponding to the changes in pH in a typical commercial sponge dough show that the sponge, which was fermented, started with a pH $= 5\cdot71$, fell to pH $4\cdot94$ after 340 minutes when it was ready to be returned to the mixer, and the finished dough then became pH $5\cdot53$ and the bread pH $5\cdot42$. In a straight dough the pH varied continuously from $6\cdot16$ down to $5\cdot66$ in the baked loaf. Rumsey (*Amer. Inst. Baking*, 1922, *Bull.* No. 8) points out that the optimum hydrogen-ion concentration for flour diastase, pH $4\cdot7$, is seldom reached during the fermentation of a normal dough, though the increase in acidity during fermentation in the range of pH 6 to 5 has the effect of considerably increasing the production of maltose toward the latter part of fermentation. As temperature has a considerable effect in the control of diastatic action in dough, the higher temperature at " proving," coupled with the lower pH, makes the effect of diastase more pronounced during the later stages of fermentation. This enables the diastase to convert starch into sufficient reducing sugars for the yeast to complete the aeration of the loaves. It is also largely upon this stage that the kind of " oven-spring " obtained depends, for if the gas production in the dough just before placing in the oven is poor there will result small, solid, unsatisfactory loaves.

There is another advantage to be obtained by bringing the dough as near as possible to pH 5 in the fermentation process. It happens that the activity of rope-producing organisms, *e.g.*, *Bacillus mesentericus*, becomes almost completely prevented. These bacteria flourish in doughs of higher pH and have been found to produce ropy doughs between pH $5\cdot5$ to $6\cdot0$. The advisability of aiming at pH 5 in dough making was first advocated by Jessen-Hansen (*Comptes rend. Lab. Carlsberg*, 1911, **10**, 170) as far back as 1911, and it has since been confirmed by Cohn and Henderson

(*Science*, 1918, **48**, 501); Dearsley (*N.Z. J. Sci. Tech.*, 1925, **8**, 34); and Dunlap (*J. Amer. Assoc. Cereal Chemist*, 1922, **7**, 2; *Cereal Chem.*, 1926, **3**, 201).

Reference will now be made to the classical experiments of Jessen-Hansen concerning the relationship which exists between the *p*H of flours, adjusted by the addition of different acids, and the sizes of the loaves which they produce when prepared by an experienced baker. Typical curves, constructed from some of his many data for different acids, are given in Fig. 98
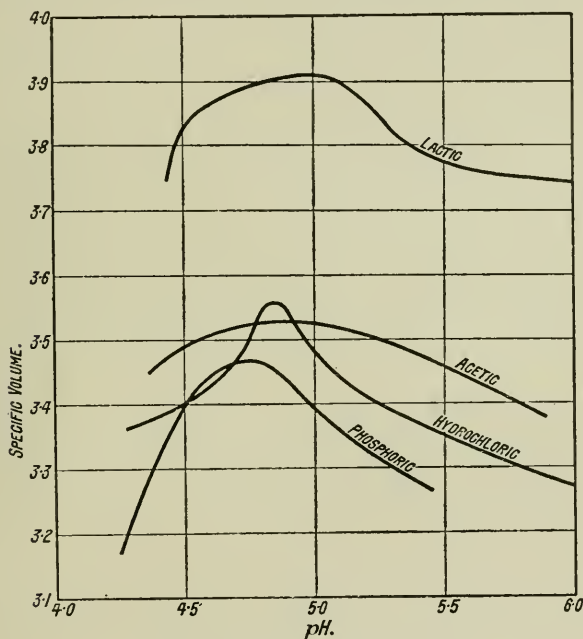
FIG. 98.—Size of Loaf and *p*H.

expressing the variation in " specific volume " with *p*H. The term " specific volume " refers to the volume in c.c. of 1 gram of bread. It will be observed that the maximum size of loaf was obtained with flours adjusted to *p*H 4·6 to 5·0. The differences in the actual maximum specific volumes given by the different acids, lactic, acetic, hydrochloric, and phosphoric, must be regarded as due to other factors, though the variation in loaf size is evidently the result of the *p*H's of the flours. He also traced the efficacy of alum as an improver to the decrease in *p*H set up in the flour.

The agents sometimes used for bleaching flour may cause

increased acidity. This applies to such substances as chlorine, nitrogen tetroxide, nitrogen trichloride, and nitrosyl chloride. Bruère (*Ann. Falsif.*, 1925, **18**, 161) suggests that pH measurement may serve as a means of detecting chlorine in flours.

The increase in the size of a moulded loaf after placing in the oven is due to the low pH attained in the dough and to the enhanced enzymic activity which occurs with increased temperature. Though the " oven·spring " actually produced depends upon such factors as the quality of gluten, the activity of the various enzymes, amylolytic and proteolytic, the kneading and moulding, there is no doubt that many of these factors are themselves dependent upon the original pH of the flour and its buffer action, *i.e.*, the resistance which it offers to increasing hydrogen concentration. Dunlap (*loc. cit.*) states that a flour having a pH of 5·7 to 5·9 will give a splendid " oven-spring." Improvers, such as acid calcium phosphate and ammonium sulphate, tend to increase the pH of flour. The physico-chemical processes involved in baking include the denaturation of the protein, a process which as shown by the work of Sφrensen is favoured by a high concentration of hydrogen-ions, and the subsequent flocculation and precipitation of the denatured protein. This, according to Sφrensen (*Ann. Brass. Dist.*, 1926, **25**, 65) takes place more rapidly at an optimum pH of 4·8.

Harrell (*Cereal Chem.*, 1927, **4**, 423) has called attention to the fact that as a rule the lowering of pH gives a much whiter bread, and for that reason sponge dough loaves are whiter than straight dough loaves. Then again, both flavour and taste of bread have some connexion with the values of the flour and dough pH.

In view of the many points which may influence the efficiency of baking, it appears probable, that, though pH does provide a valuable asset for control, the precise pH's to be attained in doughing must be fixed for each class of flour after it has been examined for such qualities as buffer content, diastatic power, gluten quality, etc.

CHAPTER XXIX.

WATER PURIFICATION, CORROSION, AND SEWAGE DISPOSAL.

THE introduction of the control of hydrogen-ion concentrations of water dates from 1921, when Wolman and Hannan (*Chem. and Met. Eng.*, 1921, **24,** April) directed attention to its importance. The chief use lies in the control of clarification processes, involving the addition of either alum or iron salts or both, to turbid and coloured waters, and in the case of boiler-feed water to establishing a pH value which will diminish its corrosive action. Another point of importance in regard to public water supply is the fact that water of low pH is apt to assist the growth of iron-bacteria, which cause incrustation of the pipes and may especially attack cast iron thereby inducing a " spongy disease " (*cf.* Ellis, *Engineering*, 1921, **112,** 457).

The reaction of water is largely due to equilibria between free carbon dioxide and bicarbonate-ions, kept in solution in conjunction with calcium and magnesium-ions, so much so that Greenfield and Baker (*Ind. Eng. Chem.*, 1920, **12,** 989) have evolved a method by which the pH of natural waters up to pH 8 may be calculated with considerable accuracy from titrations of the free carbonic acid using phenol-phthalein, and of the bicarbonate with hydrochloric acid to methyl orange. According to Kolthoff (*Z. Untersuch. Nahr-Genuss.*, 1922, **43,** 184) the pH of a saturated solution of calcium carbonate is 10·2, and the author has found that 0·001 M.-$CaSO_4$ solution does not yield a precipitate with 0·01 N-Na_2CO_3 even though a pH of 10·3 is attained. Using 0·01 M.-$CaSO_4$ and 0·1 N-Na_2CO_3, however, precipitation began at this stage. Kolthoff advocates the use of bromocresol purple for the pH determinations of water within the range pH 6·0 to 6·8, which is the range for normal natural waters.

Sea-water generally has a higher pH value. Thus, the water near the British Isles is about pH 8·2, though it undergoes seasonal variations due to the photosynthetic action of plankton. It has been shown that the greater part of the alkalinity of sea-water is produced by the more soluble carbonate, that of magnesium,

though W. R. G. Atkins (*Sci. Proc. Roy. Dublin Soc.*, 1922, **16,** 380) has found as high a value as pH 9·7, probably due to the removal of carbon dioxide by algæ. This considerable buffer action, caused by $HCO_3' \rightleftharpoons H^{\cdot} + CO_3''$, is so great in natural waters and soil extracts that it prevents the attainment of a pH value of 10·0, required for the precipitation of the magnesium hydroxide which they contain. The expulsion of carbon dioxide from tap-water by boiling leads to a higher pH value. Thus Atkins (*Nature*, 1921, **108**, 339) obtained an increase from pH 6·8 to pH 8·5.

It is difficult to obtain as high a pH as 10, though when water has been so adjusted the excessive sodium hydroxide-content has a deleterious effect when used for steam raising in rendering the metal of the boiler brittle. According to Parr and Straub (*Ind. Eng. Chem.*, 1927, **19,** 620) caustic embrittlement of boilers, resulting in cracks and crevices, occurred with those waters which contained high proportions of the carbonates of sodium, magnesium, and calcium. Such water, though containing too little free alkali to cause direct embrittlement, has been found to lead to the production of solid caustic soda in the cracks and crevices. It is probable that water which has been softened either by sodium carbonate or by the action of permutite will contain sodium salts in fairly high concentrations.

It has been recently shown that the hydrogen-ion concentration of brine used in reviving used permutites is an important factor. Moreover, the pH of the water undergoing softening affects the zeolitic action. Too high a pH value, above pH 7·8, leads to unsatisfactory results, and too low a pH has a solvent action on the agent (Sweeney and Riley, *Ind. Eng. Chem.*, 1926, **18,** 1214). Despite the fact that zeolite action is restricted to a pH range from 6 to 8, which is lower than that at which magnesium hydroxide or basic carbonate become precipitable, it happens that, due to the formation of insoluble calcium and magnesium complexes with the permutite, a large proportion of these metals thereby get removed from the water. In this method of softening, the softened water instead of having its bicarbonate in combination with calcium and magnesium has it in conjunction with sodium.

We shall now consider what advantages have been found to arise from the pH control of the alum treatment of water. The maximum clarification depends upon the nature of the aluminium hydroxide precipitate formed in the water on treatment with lime or some other alkali. Another point is that of the economic use of alum. Precipitation is determined largely by the pH set up, though as we have seen in Chapter XV. the actual appearance

of the precipitate is dependent upon the nature of the anion in solution. Thus from an aluminium sulphate solution precipitation began at about pH 4·1, whereas from chloride solutions though the pH curves were similar, the formation of precipitates was delayed until about pH 6. Moreover, organic radicals in the solution sometimes prevented the separation of a precipitate altogether (see Chapter XVII.). It is therefore surprising to find that different workers have advocated different pH values as leading to the best precipitation.

The results of Theriault and Clark (*U.S. Pub. Health Rep.*, 1923, 181) show that as the alum solutions become increasingly dilute, the pH range in which rapid flocculation occurs rapidly becomes narrower, giving a maximum flocculation at pH 5·5. Hatfield (*J. Amer. Water Works Assoc.*, 1924, **11,** 554) found the maximum rate of flocculation with alum in Lake St. Clair water took place at pH 6·1 to 6·3, but the filter effluent was found to be free from soluble aluminium salts over a wider range, from pH 5·8 to pH 7·5.

Miller (*U.S. Pub. Health Rep.*, 1925, 351) has carried out some very useful work on the nature of " alum floc," and also on the amounts precipitated at different pH values from very dilute solutions containing various anions. His results are summarised in Fig. 99. The continuous curves refer to precipitations from solutions 0·005 Molar with respect to Al. The precipitant was sodium hydroxide, except in one instance when potassium carbonate was used. The discontinuous curves correspond to precipitations from 0·0005 M.-Al solutions with sodium hydroxide. It will be observed that the zone of maximum insolubility of the aluminium hydroxide precipitated from a sulphate solution was considerably more extensive than that obtained from a chloride solution. The widening of the zone by the inclusion of ammonium chloride in the solution is noteworthy, and explains the importance of that salt in " salting out " the colloidal alumina in analytical procedures. The effect of dilution is also clearly indicated, not only in reducing the insolubility zone, but also in permitting a certain amount of aluminium hydroxide to remain in solution, presumably in colloidal form. Miller found that the rate of precipitate formation from a very dilute alum solution attained a maximum value at about pH 5·5, whereas from a chloride solution this occurred at pH 8·0. This demonstrates the strong coagulating power of the sulphate-ion.

For the successful clarification of water by alum three factors must be considered : (1) the minimum amount of alum to be added must be known, (2) there must be present an anion which

will readily promote coagulation, and (3) the correct pH value for a particular water must be established. As regards the first factor a saving may be effected by merely adding the minimum amounts and adjusting the water to the required pH value by the addition of sulphuric acid or alkali.

From what has been written, it will be understood that pH control alone may be of comparatively little value, and will certainly provide no panacea for the troubles encountered in water treatment. If, however, it be carried out with a full know-
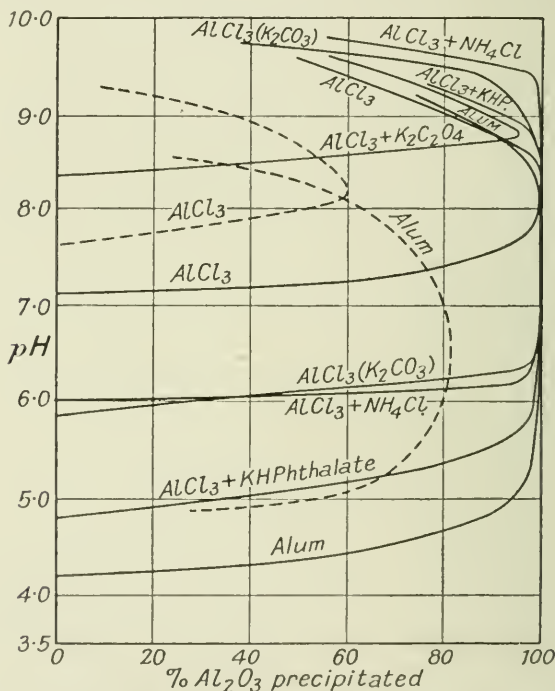
FIG. 99.—Effect of pH and Anions on the Precipitation of " Alum Floc ".

ledge of the contents of the water, then it constitutes a most valuable method of control. If a pH as low as 5·5 has been adopted, it is often found that the filtered water is corrosive, and that consequently its pH must be raised by means of sodium or calcium hydroxides.

Parker and Baylis (*J. Amer. Water Works Assoc.*, 1926, **15**, 22) have devised a pH control apparatus, using the tungsten electrode, by which, not only can an automatic and continuous record of the hydrogen-ion concentration of the treated water be obtained

but also the addition of lime to bring the water to some desired
pH after filtration can be effected. Parker and Greer (*ibid.*, p. 602)
have designed apparatus for the pH control of boiler feed water
which they consider to be undoubtedly the cheapest method
available for its systematic control, and by which the chemical
dosage is not merely made proportional to the flow, but also is
made in such proportions as to compensate roughly for the acidity
or the amount of scale forming, or for corrosive salts present.

The pH value of water appears to be of fundamental importance
in regard to its sterility. There seem to be some grounds for the
belief that bacteria of the colon and typhoid group are destroyed
in media of pH greater than 9·5. A natural water which has been
softened by treatment with the correct amount of lime to form
calcium carbonate will have a pH value in the region of 9·5.

Ferrous sulphate is sometimes used in place of alum, but as
will be seen from Fig. 61 on page 254 ferrous hydroxide, or, better
basic sulphate, is not completely precipitated until a pH of about
9 is reached. Ordinary natural waters are seldom of this pH, and
consequently such a treatment would involve a subsequent alkali
treatment.

Soluble aluminates, namely those of potassium and calcium,
are finding application in water treatment (Barnett and Haux,
Can. Eng., 1926, **51,** 725, and Bardwell, *J. Western Soc. Eng.*,
1926, **31,** 392). The use of these necessitates control of the hydro-
gen-ion concentration to ensure the best clarification. Though the
solutions themselves have pH values lying between pH 10 and 11,
considerable quantities would have to be added to raise the pH
of the water to 10, and so bring about the precipitation of mag-
nesium hydroxide. Nevertheless Bardwell has found that sodium
aluminate does decompose magnesium salts present and reduces
the scaly material to 1 to $1\frac{1}{2}$ grains per gallon.

Corrosion.

The treatment of water that it may have the minimum corrosive
action on the metal surfaces with which it comes into contact is
of paramount importance. This difficulty arises not only in
connexion with service pipes but also with boilers and heating
systems.

Among the factors involved in the process of corrosion of a
metal are the following : (1) the normal electrode potential of the
metal and its hydrogen overvoltage, and the manner in which these
are influenced by the impurities present in the metal ; (2) the
hydrogen-ion concentration of the water ; (3) whether there are
any metals in electrical contact, and if so, their electrochemical

nature ; (4) the oxygen and salt contents of the water ; (5) the ease with which any hydrogen liberated at the metal surface is removed, especially by any possible catalytic oxidation, by the dissolved oxygen or other oxidising agents ; (6) the presence of possible passivating agents ; and (7) the pervious nature of the oxide film to oxidising agents.

We shall concern ourselves here only with the influence which the hydrogen-ion concentrations of water may have on the corrosion of iron. Since acids have a solvent action on iron, their corrosive action may be represented by the reaction

$$Fe + 2H^{\cdot} \rightleftharpoons Fe^{\cdot\cdot} + H_2.$$
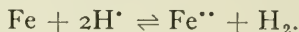
The direction taken by this reaction will be determined by the pH of the water, and the electrode potential of iron together with its hydrogen overvoltage. The continued reaction towards the right will be determined by the ease with which the hydrogen gas film can be removed from the surface, either mechanically or by oxidation. Furthermore, this will depend upon the nature of any oxide or, better, hydrated oxide film which may have been deposited on the surface. Such a film may have a distinct protective action. The formation of the film depends upon the concentration of ferrous-ions which has been produced, and whether this and the hydroxyl-ion concentration of the water will be sufficient to exceed the solubility product of ferrous hydroxide. Once this film has been formed at the metal surface, its character will depend upon its subsequent oxidation to the less soluble ferric hydroxide.

Sweeney (*Trans. Amer. Electrochem. Soc.*, 1928, **53,** 317) has calculated from thermodynamic considerations that even in the absence of oxygen there is a small driving force tending toward the formation of ferrous hydroxide and hydrogen according to the equation :

$$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2 \text{ (1 atmos.).}$$

Once this reaction has proceeded to an extent that the solubility product of ferrous hydroxide becomes exceeded, then the magnitude of the driving force (*i.e.*, the capacity of the reaction for doing external work) should be independent of pH of the solution with which the iron is in contact. The rate of corrosion, however, will depend, among other things, on the pH, the hydrogen overvoltage, diffusion through the surface film, and catalytic effects. Using Britton's data concerning the precipitation of ferrous hydroxide (see p. 254), he has obtained a curve connecting the pH of solutions with the concentrations of iron dissolved, which is in remarkable agreement with the solubility of iron in natural waters

of differing pH values as found by Baylis (*Ind. Eng. Chem.*, 1926, **18**, 370).

Wilson (*Ind. Eng. Chem.*, 1923, **15**, 127) found that iron underwent rapid corrosion when immersed in solutions of pH less than 4·3. Here the hydrogen overvoltage was the controlling factor, and the effect of the dissolved oxygen was negligible. When iron was immersed in an acid solution of pH greater than 4·5 appreciable amounts of hydrogen began to appear, first as dissolved gas, but in solutions of about pH 4 bubbles of hydrogen became perceptible. When iron is placed in contact with other metals of low hydrogen overvoltage, this gas evolution may often begin in solutions of higher pH, but it must be remembered that the hydrogen-ion concentration still remains one of the controlling influences. At pH values higher than 4·3 iron becomes covered with a protective coating. The extent of the protection afforded again is largely a question of pH. From about pH 5 to about pH 10·5, this layer permits the passage of dissolved oxygen through it which thereby enables corrosion to take place, though at a somewhat reduced rate. In the more alkaline solutions the hydrogen produced at the surface becomes negligible, though the effect of oxygen on the film becomes more marked. This yields a more resistant coating, and as a consequence corrosion becomes further reduced. Thus it follows that as far as actual corrosion is concerned, the amount of dissolved oxygen removed from water may be regarded as a measure of the extent of corrosion in any given time. Whitman, Russell, and Altieri (*ibid.*, 1924, **16**, 665) found that the equation : $3O_2 + 4Fe \rightarrow 2Fe_2O_3$ represented the reaction to the extent of about 95 per cent. They therefore carried out experiments in which oxygen ladened-water, adjusted to various pH values by means of either hydrochloric acid or sodium hydroxide, was allowed to flow at a uniform rate, about 2·2 litres per minute, through a steel box having baffle plates with a total surface of 17,400 sq. cms. From determinations of the oxygen contents of the influent and effluent waters, the amounts removed through corrosion in a given time could be ascertained. Fig. 100, showing the amounts of oxygen removed from each litre of water at different pH values, indicates the influence of temperature in accelerating corrosion, and also that the corrosive attack was considerable in acid solutions below pH 5. Between pH 5 and 9 the extent to which corrosion took place was not greatly affected by the hydrogen-ion concentration, except that it was not entirely prevented. Above pH 9 the effect of enhanced alkalinity becomes evident in rendering the rust film more protective. Similar conclusions have been arrived at by Shipley and McHaffie
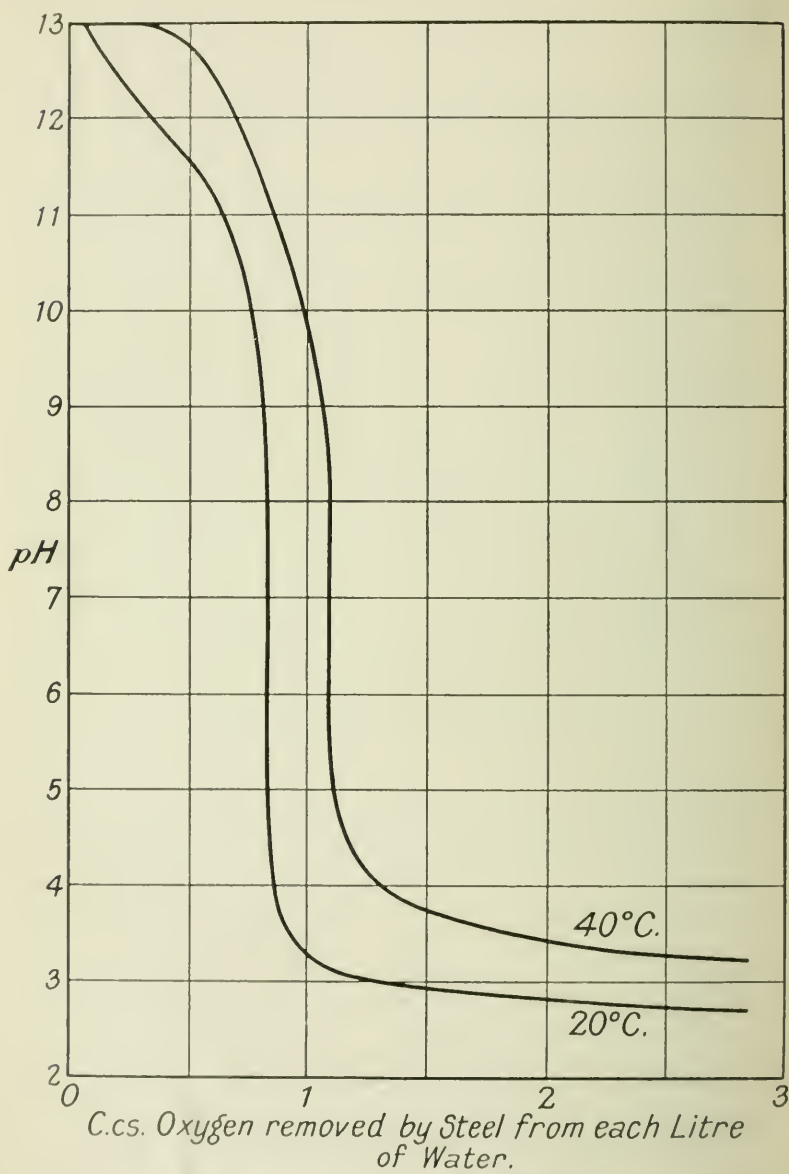
FIG. 100.—Corrosion of Steel by Oxygenated Water.

(*Can. Chem. Met.*, 1924, **8**, 121), who found that corrosion of iron in the absence of oxygen is proportional to the hydrogen-ion concentration up to pH 9·4, at which point the evolution of hydrogen gas almost ceases.

Hydrogen-ion concentration is also an important factor in the corrosion of other metals. For instance, water of too low a pH value, such as may be produced by the addition of too much alum, or has been obtained from swampy areas where it has become contaminated with decomposing organic matter, will be particularly corrosive to lead, zinc, and aluminium. Such water when conveyed through lead pipes may lead to lead-poisoning. Protective coatings of hydroxide or basic carbonate are usually formed on metals in contact with waters of high pH. In cases of metals capable of forming amphoteric hydroxides, *e.g.*, aluminium and zinc, corrosion also is set up by waters of high pH. Thus with galvanised vessels and pipes corrosive action is at a minimum at pH 9·5 to 10.

Sewage Disposal.

The chief processes involved in the activated sludge method of sewage disposal are (1) digestion and (2) treatment to effect the further precipitation of solid matter and thereby to facilitate filtration. In both these processes control of hydrogen-ion concentration has been found of great service.

In the digestion process, the so-called " activated sludge " is produced. It consists of flocs due to microbial growth, which has been assisted and accelerated by aeration of the sewage. This sludge, after being allowed to settle, is separated by decantation and the remaining liquor is mixed with fresh sewage and again subjected to air treatment. In this process some of the matter is oxidised and passes away as carbon dioxide, whereas under certain conditions bacterial action promotes reduction resulting in the evolution mainly of methane, though occasionally higher hydrocarbons and hydrogen are formed. As a result of these complicated reactions, humus together with other organic matter becomes precipitated. Sometimes it is desired to give badly digested sludge a further treatment, so as to bring about a separation of colloidal matter from the liquor. Incidentally, where it is desired to dry the sludge for use as manure it is found that the insoluble matter deposited in the aeration tanks is too much swollen through the imbibition of water. The water-content can be reduced by the same treatment accorded to poorly digested sludge.

Considerable attention has been given by Rudolfs (*New Jersey Agr. Exp. Station*, *Bull.* No. 427), and Fair and Carlson (*Eng.*

News-Record, 1927, **99**, 881) to the *p*H changes which occur during digestion. The digestion of properly seeded sewage solids, as measured by the rate of gas evolution, normally takes place in three stages : (1) the " acid " stage, (2) a long period of very slow digestion, and (3) the " alkaline " stage, in which methane is produced. During each of these stages the measurement of *p*H provides an excellent guide of the extent to which digestion has proceeded.

The liquor in contact with freshly settled sludge from ordinary sewage has a *p*H of about 7. After standing for a few hours, the separated sludge begins to show signs of bacterial decomposition, in the form of gas evolution and the milky appearance of the liquid. The *p*H value falls to about 5, and besides the development of a foul odour the sludge becomes sticky and slimy and difficult to drain. Such a *p*H value, being very near to *p*H 4·7 the isoelectric point of many ampholytic bodies, is not conducive to the passage into solution of nitrogenous bodies. This has an inhibiting action on the process of digestion which is characterised by a low gas production, and a slowly increasing *p*H value. Under normal conditions this phase of the process requires about six months. Fair and Carlson investigated the effects produced by adjusting the *p*H values to 6·8, 7·2, and 7·6 by the addition of lime, marble dust or dolomite dust. In all cases the length of this period was considerably shortened and gasification was greatly accelerated. By adopting *p*H control the time necessary was reduced to about eight weeks. Their experiments showed that the optimum *p*H in the control of sludge digestions varies according to the stage of digestion reached by the decomposing matter. It would appear that a *p*H of about 6·8 is the optimum during the initial stage while *p*H 7·2 should be afterwards obtained.

In the third stage of an uncontrolled digestion, the *p*H rises to about 6·8 and methane production becomes active, whilst the sludge becomes non-putrid, does not foam and possesses a slight earthy or tarry odour. The formation of sludge is especially sensitive to changes in hydrogen-ion concentration. At ordinary temperature, the optimum *p*H is 7·4 (Cramer and Wilson, *Ind. Eng. Chem.*, 1928, **20**, 4). It is interesting to compare this with the fact that if the *p*H of blood is changed much from *p*H 7·4 tissue building ceases. The *p*H's of liquors are maintained by the addition of lime and by having an excess of digested sludge over the fresh solids present. Parker (*Ind. Eng. Chem.*, 1927, **19**, 660) describes an automatic *p*H control, by means of the tungsten electrode (see page 403), which has been installed at Winston-Salem, and by which the addition of the requisite amounts of milk-of-lime is manipulated and regulated.

Due to the fact that the density of sludge formed in the region of pH 7·3 is greater than that of water, through its enhanced absorption of water, the sludge sinks, and this also occurs when the sludge has not undergone complete digestion. The slimy nature of the latter renders extremely difficult the separation of the liquors, which on account of the poor digestion still contains appreciable quantities of putrefying matter,. If the pH value is brought to pH 3 to 5, it is found that not only does the badly digested sludge float but that the coagulation of a considerable amount of the organic matter occurs, with the result that efficient filtration is greatly facilitated.

Wilson (*J. Soc. Leather Tr. Chem.*, 1921, 5, 268) has applied the Procter-Wilson theory of the swelling of jellies to the filtration of activated sludge at Milwaukee. The rate of filtration was shown to be a function of the pH and was increased three-fold by adjustment to an optimum pH of 3·2. By using aluminium sulphate, however, and bringing the pH to 4·3 the rate of filtration was increased seven times. Slightly higher efficiencies are reported by Cramer and Wilson (*loc. cit.*). They further point out that the filtering efficiency of aluminium sulphate sludge adjusted to pH 4·4 increases from 7·5 to 40 times when heated to 80° C. It is interesting to find that the optimum for aluminium sludge is pH 4·4, which is, as shown on page 260, approximately the point at which basic aluminium sulphate undergoes precipitation. It is probable that the coagulating and filtering efficiency is due to the buffer action of basic aluminium sulphate during precipitation which thereby enables a pH to be established quite near to the isoelectric point of most organic bodies. The action seems to be identical with the tanning action of basic aluminium sulphate, which in effect, is probably nothing more than the mutual precipitation of two colloids.

When filtration becomes more difficult through low temperature in winter-time, Cramer and Wilson found that the adjustment of the pH of the sludge to what they regard as its isoelectric point, namely pH 3·4, with ferric chloride, instead of sulphuric acid, there results an increase in filtering efficiency of thirty times the normal rate. Such an increase makes the operation of the plant possible. At Milwaukee more than a million gallons of sludge, drawn from over 85 million gallons of sewage, are so treated per day. This sludge is converted into excellent dry fertiliser to the extent of 100 tons per day.

Similar considerations apply to the disposal of industrial wastes, *e.g.*, the effluents from tanneries, textile-mills, creameries, especially in regard to the efficiency of the various coagulants used.

CHAPTER XXX.

THE BEARING OF HYDROGEN-ION CONCENTRATION ON THE FERTILITY OF SOILS.

pH and Soil Chemistry.

The extensive application, during the last ten years, of the principles of pure science to the study of the complex phenomena involved in soil management and cropping has emphasised the importance of the hydrogen-ion concentration of the soil as a factor in its fertility. The recognition of " sourness " in soils and of the common remedial measures of liming, chalking, or marling doubtless dates back to the earliest days of systematic husbandry. The less extreme variations in soil reaction in the accompanying and less obvious effects on crop yield have been the subject of scientific inquiry only in very recent years. Definite attempts to correlate soil " sourness " with the presence of acids have, however, merely served to emphasise the wide scope and complexity of the general problem. In a few extreme cases it has been recorded that soils have indicated the presence of acid substances directly by the reddening of moist blue litmus paper, but by far the greater number of soils which to the practised eye of the agriculturist are sour fail to demonstrate their acidity in so simple a manner. The relatively enormous volume of recent research work, whilst throwing much light on the chemical processes concerned in the souring of soils, has not yet brought either a clear conception of the numerous contributing causes or the *modus operandi* of their manifold effects.

The recognition of the extreme sensitiveness of the majority of living organisms to changes in the alkalinity or acidity of the media in which they live and from which they obtain their food materials, has profoundly affected our conception of the mechanism of plant growth. Changes in the hydrogen-ion concentration in the soil not only affect the plant directly, but also modify both the physical and chemical conditions of the soil and the distribution and activity of its teeming population of micro-organisms. Each of these latter factors in turn may indirectly affect the nutri-

tion of the plant. We will now consider more fully some of the effects above mentioned.

Hydrogen-Ion Concentration and Plant Growth.

Detailed study of the nutrition of a number of plants has shown a very close relationship between crop yield and hydrogen-ion concentration of the nutrient solution. Generally speaking, there is not only a definite range of pH values outside of which the plant will not grow at all, but also a much narrower range corresponding to the region of optimum growth. The work of O. Arrhenius shows that graphical representations of the relationship between crop yield and the reaction of the nutrient media are of the form illustrated in Fig. 101.
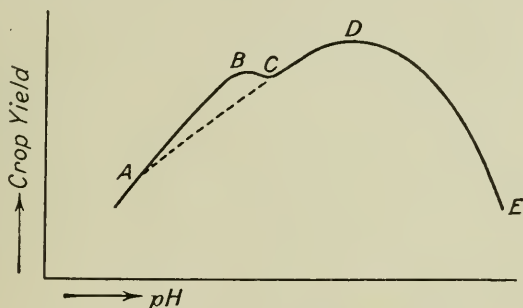
FIG. 101.—pH of Soils and Yield of Crops.

The characteristics of these growth curves are—
(1) A fairly wide range of *possible* growth.
(2) A relatively narrow range of optimum growth.
(3) A more rapid falling off of crop yield on the alkaline side of the optimum, *i.e.*, a steeper curve, than on the acid side.
(4) In many cases a secondary maximum in the curve, *i.e.*, the portion ABC, lower than the principal optimum CDE.
The extreme range of pH values in ordinary soils is from pH 3·5 to 8·0. Few, if any, plants can grow outside this range, and very few can withstand the conditions obtaining in the whole range of pH values within these limits. The work of Olsen (*Compt. rend. Lab. Carlsberg*, 1923) indicates that the growth range of individual species of plants is generally restricted to 3·5 units of pH, with optimum conditions over ranges of 0·5 to 1·5 units. Naturally the majority of our existent species of plants have an optimum range of pH 6·5 to 7, this being a mean value in our arable soils. Typical acid-loving plants have an optimum range

of pH 4·5 to 5, and at values approaching the neutral point become stunted and chlorotic. Plants that flourish in neutral soil seldom thrive at pH values greater than 7·3 to 7·4, and from pH 7·5 upwards growth is more or less restricted to aquatic or semi-aquatic plants.

The following table shows the growth ranges and optimum ranges of pH values for a number of common agricultural crops grown under artificial nutrient conditions, that is, under conditions in which adequate nutrient material is supplied throughout and only the actual pH values are allowed to vary.

TABLE 101.

OPTIMUM pH RANGE FOR GROWTH OF COMMON CROPS.

Crop.	Growth Range pH.	Opt. Range pH.	General Remarks.
Potato	—	5·0–5·5	Uninjured at 4·2
Barley	6·5–8·0	6·4	—
Oats	—	5·3–5·8	Injured at 4·3
Wheat	5·2–7·0	—	—
Rye	4·2–7·6	6·2	—
Turnips	5·0–6·5	6·0–6·5	—
Lucerne	6·0–7·2	7·0	—
Sugar beet . . .	—	7·0–7·2	—
Pasture grasses (average) .	5·0–6·5	6·0	—
Sugar cane . . .	—	7·0	—
Tea	—	5·4	—

It is interesting to observe that even among these agricultural crops selected over generations to suit soils not varying greatly from the neutral point still show a considerable variation in the optimum growth ranges.

A further point of interest, not apparent in the above figures, is that although the optimum ranges of pH for a number of plants may be similar it does not follow that the growth ranges are similar or that injury is observed in soils of similar pH. Thus Olsen has recorded that the optimum ranges for three typical crops are—

Lucerne   .   .   .   . 6·5–7·0
Rye   .   .   .   . 6·0–6·5
Buckwheat   .   .   . 6·0–6·7

yet at pH 4·0 the crop yields of these three plants expressed as percentages of the respective optimum yields are—

Lucerne   .   .   . 13 per cent.
Rye .   .   .   . 82 ,,   ,,
Buckwheat   .   . 90 ,,   ,,

The figures quoted above relate to plants grown under strictly controlled laboratory conditions, in which the only variant is the pH value of the nutrient medium. When we come to examine plants growing under natural conditions in soil the effects of variations of reaction are less easy to trace. The solubility or availability of the mineral nutrients of the soil are marked by, or influenced by changes in the pH value, and the direct effect of the latter on plant growth becomes merged into the effect of changes of nutrition. As a result, the apparent optimum pH range for a particular plant growing in one locality may differ considerably from that of the same plant growing elsewhere. Moreover, the effects of differences in temperature, amount and rate of water supply to the plant roots, hours of sunshine, together with other climatic and regional conditions become operative. Under natural conditions, therefore, the relationship between soil reaction and plant growth becomes to some extent specific to local conditions. This point becomes of considerable importance in evaluating the lime requirement of soils (see later). The effect of local conditions on the apparent optimum pH range on plant growth for a number of farm crops is well illustrated by von Kreyberg. Table 102 shows the apparent optima in (1) a humid climate, (2) moist climate and light sandy soil.

TABLE 102.

OPTIMUM pH RANGES FOR PLANT GROWTH IN DIFFERENT CLIMATES.

Crop.	Soil (1).	Soil (2).
Wheat	7·3–7·8	6·4–6·9
Barley . . .	7·6–8·2 4·1–6·5	6·2–6·9
Sugar beet . . .	7·6–8·5	6·6–7·3
Red clover . . .	8·3–8·7	6·0–6·8

The interrelationship between plant growth and soil reaction, coupled with the fact that the optimum ranges of pH for the growth of plants varies with the species, is the primary basis of certain peculiarities in plant distribution long recognised by the practical agriculturist as indications of sourness in soils. There is, of course, no sharp line of demarcation between the natural herbage of soils of different reaction value. Nevertheless a relatively small change of, for example, 1 to 2 units of pH value is sufficient to retard the growth of certain types of plants and to

encourage others to a corresponding extent, and the relative pro-
portions and fullness of growth of certain plants frequently
furnish information to a close observer as to the degree of " sour-
ness " obtaining in a particular soil.

Among the " tell-tale " weeds of sour soils are spurrey, sheeps'
sorrel, sourdock, bedstraw, and bracken. Spurrey is a fairly
sensitive plant to reaction changes, but the distribution of the
remainder is fairly general. There is, however, a notable increase
in the numbers and size of fundamental plants on acid soils, which
makes these species of value in indicating acid conditions. More
important than any of these, in connexion with sour soil indicators,
is clover, and in particular the wild white clover. In this case,
soil acidity is marked by the complete absence of the plant among
the natural herbage. It would seem, however, that even in sour
soils, seed or rootstocks remain dormant for lengthy periods, for
in the majority of cases treatment of sour soils with lime or more
generally with basic slag, results in the appearance of a considerable
plant of white clover in the ensuing season. The value of clover
and of leguminous plants generally in the nutrition of animals
renders their presence in herbage a matter of very great import-
ance. As a result, much of the economic interest in the reaction
of meadow land and pasture has centred round its effects on the
growth of clover.

Soil Micro-organisms and Hydrogen-Ion Concentration.

Even more sensitive than plants to changes in soil reaction are
the soil bacteria, and among these none are more necessary to plant
growth than the various species concerned in what is usually de-
scribed as the " Nitrogen Cycle," viz.; that continuous succession
of processes in which nitrogen becomes in turn a nutritive sub-
stance of plant, animal, and soil organism. Generally speaking
acidity tends to retard the activity of soil bacteria, which although
capable of existence and even of slight activity over nearly the
whole range of normal pH values in soil, have a range of optimum
activity narrower than that of plants. The growing plant absorbs
its nitrogenous food material in the form of nitrate and the trans-
formation of the protein matter of animal and vegetable waste to
nitrate is entirely a biological function, and depends on the ac-
tivities of a succession of organisms each concerned in one of the
usually accepted stages of transformation of organic nitrogen →
ammonia → nitrite → nitrate.

The various organisms involved in these changes are differently
affected by changes in soil reaction. Figs. 102 and 103 are typical

representations of the relationships between pH values of soil
and the activity of (a) organisms such as *B. Mycoides*, *B. Fluores-*
cens, *B. Caudatus*, and probably some fungi which bring about the
transformation of organic nitrogen compounds to ammonia, and
(b) those such as *B. Nitrosomonas*, converting ammonia to nitrate,
and *Nitrobacter* respons-
ible for the major trans-
formation to nitrate.

FIG. 102.

It is to be observed
that in the neighbourhood
of the neutral point the
ammonifying organisms
have optimum activity,
whilst the nitrate pro-
ducers have not yet
reached optimum pro-
ductivity. Nevertheless the rate of conversion of ammonia to
nitrate is so much greater than the preceding change that in normal
soils little or no ammonia is found. A small change of pH toward
the acid zone results in a relatively small decrease in ammonia
production, but a very substantial reduction in nitrate formation
with the result that under milder acid conditions there is a ten-
dency for ammonia to accumulate. Moreover, since ammonia is
not available as a nutrient to most plants, we have here an illustra-
tion of one of the several indirect ways in which acidity in field
soils tends to retard the growth of plants. Direct observation shows
that in soils of pH greater than 6·5 nitrification proceeds more
rapidly than ammoni-
fication. In the region
of pH 6·5 to 6·0 the
rate of the two pro-
cesses approach each
other closely. In most
soils at pH 5·5 there is
a distinct accumulation
of ammonia, and in the
region of pH 4·5 nitri-
fication has practically
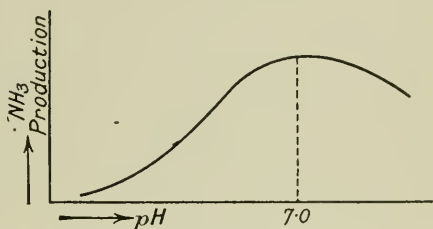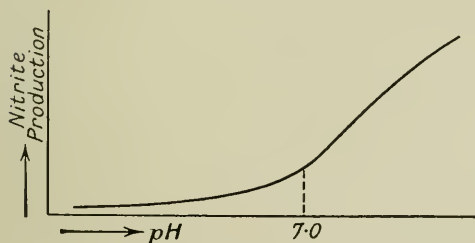
FIG. 103.

ceased. The ammonifying organisms are, however, still active
though at a somewhat reduced rate and even at pH 3·5 are able
to carry out their particular function.

Perhaps the most sensitive among the organisms of the nitrogen
cycle are those capable of fixing the free nitrogen of the atmo-
sphere, *viz.*, the several species of *Azotobacter* and the *Clostridium*

Pasteurianum. Gainey showed that among a great number of soils examined by him, that those having *p*H values less than 6·0 were invariably free from nitrogen-fixing organisms, whereas all soils more alkaline than *p*H 6 contained these organisms.

Inoculation of the more acid soils with cultures of the organisms failed. Fixation of nitrogen proceeds but slowly in soils of *p*H 6·0 to 6·8. From 6·8 to 7·0 there is a sharp acceleration in the activities of these bacteria and an optimum condition exists at about *p*H 7·1 to 7·2. So remarkable is the rapid increase in nitrogen fixation with change of *p*H from acid conditions to the neutral point that it has been suggested that the nitrogen-fixing organisms might well be utilised as indicators in the determination of the lime requirement of soils (*i.e.*, the amount of lime necessary to eliminate " sourness " in soils). Although this process has not been generally adopted it nevertheless provides information of practical value, and, as a biological test finds favour among some investigators as being independent of any theory of the chemical nature of soil acidity.

Still another class of bacteria concerned in the nitrogen cycle are those species of organisms capable of reducing nitrites and nitrates in soil, the nitrogen of which very largely reappears as the free element. Fortunately these organisms are of lesser significance in arable soils, but under certain conditions, *e.g.*, in water-logged soils where soil aeration is impossible, the denitrifying organisms may become active. A number of species is involved, but generally speaking they may be classified according to whether they utilise nitrites or nitrates in their metabolic processes. The former class has been less thoroughly examined, but it is established that they are most active in mildly acid soils, having an optimum range of *p*H of 5·5 to 7·0. Their activity ceases at about *p*H 7·3, but on the acid side of the optimum the range seems more extended. The second class of organisms is differentiated by being more favoured by alkaline conditions. The optimum range is *p*H 7·0 to 8·1 ; at *p*H 6·1 to 6·4 their activity has become very low and at *p*H 5·5 on the one side and *p*H 9·8 on the other reduction of nitrates ceases altogether. The difference in reaction ranges of these two types of reducing bacteria serves to explain the accumulation of nitrates in certain waterlogged soils and not in others.

If the pasture on acid land is examined closely it will frequently be found that instead of a firm soil surface immediately beneath the growing grass, there is a matted layer of half-decayed grass stems —the accumulation of, perhaps, many years. In sweet soils these grass residues rot down and become an intimate part of the soil.

This is the result of certain classes of cellulose-destroying organisms which convert the tissues of the grass into the dark spongy " humus " characteristic of the appearance of a well-rotted manure heap. Examination of the top soil of a healthy pasture shows it to be considerably darker in colour than the subsoil, due to the steady accumulations of humus matter. The organisms bringing about the decomposition of cellulose have an optimum range of activity of pH 6·8 to 7·5 and are sharply affected by slight acidity, becoming almost inactive at pH 6·0 to 6·5. The result of their inactivity is manifest in the " mat " of grass residues characteristic of acid pasture. In practice this " mat " can never be satisfactorily cleared until the cellulose-splitting organisms can be stimulated into activity by suitable adjustment of the soil reaction. The preparation of " artificial farmyard manure," which in recent years has closely followed the work of Hutchinson and Richards at Rothamsted, affords yet another example of the importance of regulating the reaction of the medium in order to maintain the vitality of the cellulose-splitting bacteria. The process is essentially a large scale representation of what happens in the surface soil of pastures. The nitrogen which these organisms need is supplied artificially, but unless the reaction of the fermenting mass of cellulosic material is maintained neutral or slightly alkaline the process of cellulose conversion becomes slow or practically ceases, the stack does not " heat " sufficiently and the product is of a very inferior quality.

Soil Reaction and Plant Disease.

In yet another sphere soil reaction may influence the yield of our agricultural crops, *viz.*, in its effect on the incidence or severity of many plant diseases. At the moment there is very little detailed information on this point, but it is a safe prediction that a more general understanding of this question will become a powerful weapon in the hands of those who seek to control the fungus and bacterial diseases of plants. Probably the best-known instance of the interrelationship of soil reaction and plant disease is that of " Finger and Toe," which is so prevalent in kale, cabbage, swedes, and other plants of the order *Brassicæ*, when grown on acid soils. This disease is extremely rare in neutral or alkaline soils, but is extremely persistent on acid soils. Even the common practice of avoiding disease by including susceptible crops in rotations at long intervals fails in this case. So far as is known the only safe remedy lies in correcting the soil reaction. As a result of the extreme sensitivity of this disease to soil reaction its appearance

has long been regarded as an infallible indication of sourness. Again both wart and scab diseases of potatoes are well known to be far more prevalent in neutral and alkaline soils than in acid ones, and this, coupled with the fact that the optimum growth range for potatoes is below pH 6·0, is strong evidence in support of the long-established practice in cropping of " keeping lime and potatoes as far apart as possible " in the rotation. As examples of more recent investigations on the correlation of plant disease and soil reaction may be mentioned the work of Sherwood on the *Fusarium* wilt of tomatoes. This disease is most prevalent in acid soils, but by the addition of increasing amounts of lime the percentage of attacked plants was steadily reduced to a minimum, which corresponded with a soil reaction of pH 7·4. Again the black root rot of tobacco has been shown to cause severe injury to plants growing in soil of pH greater than 5·9, whereas on soils with pH less than 5·6 the disease is rare, and even when observed does little damage. Instances of preliminary investigations of this kind might be multiplied at great length but the whole question is little understood, and cause and effect are in many cases not easy to distinguish. Doubtless in many cases, the disease organisms are directly influenced by changes in soil reaction, but it must also be borne in mind that variations of reaction even when not far removed from neutrality may profoundly alter the conditions of plant nutrition ; and this, in turn, does much to weaken the plants' natural resistance to infection. This phase of the general question of soil reaction is one which invites deeper investigation with every assurance of fruitful results.

Theories of Soil Acidity.

From the above it is seen that the reaction of a soil is intimately connected with plant growth in a number of ways, and that any marked deviation from the neutral point brings with it the probability of decreased crop yields which become more and more affected as the pH value of the soil diverges from the range 6·5 to 7·0. Extremes of soil reaction on the alkaline side are relatively less widespread, and, moreover, the causes, rectification, and effects on plant growth bring the investigator into spheres of physico-chemical inquiry in which hydrogen-ion concentration plays little part. The so-called " alkali " soils will not, therefore, be considered here. The consideration of acid soils, and the measurement of acidity, for the purpose of arriving at satisfactory ameliorative measures, has demanded much more detailed investigation, and in this matter the measurement of

hydrogen-ion concentrations has figured largely. The experimental aspect of soil acidity, itself a complex problem, is rendered more difficult by the impossibility in many cases of the isolated study of a particular series of changes, with little or no measured control of interdependent reactions and effects. As a result existing theories of soil acidity are largely the outcome of repeated attempts to correlate experimental data which in many cases have no common basis. The International Society of Soil Science has done much to bring together the widely scattered soil scientists of the world and to derive from discussion clearer ideas on many soil problems. The reports of the Society on the meetings at Gröningen in 1926, when the whole problem of soil acidity was given much consideration, are an important milestone in the progress of this branch of agricultural chemistry. It can hardly be stated that we have arrived at a clear-cut understanding of the detailed chemistry of soil acidity, but we have, to say the least, gone far towards reaching generally accepted ideas which can form the foundation of practicable methods of measuring and explaining the nature of soil reaction.

It is both interesting and instructive to recall some of the theories put forward from time to time in explanation of the phenomena of " sourness " in soils. The presence of free mineral acid in soil has long been discredited even when coupled with the selective absorption theory. The occurrence of organic acids can, however, be definitely proved and offers a somewhat more practicable basis of consideration. In highly organic soils acidity may be partially or wholly the result of the presence of such bodies.

The degree of acidity of organic soils, is, generally speaking, much smaller than in many mineral soils where only small amounts of organic matter exist. Moreover, recent work shows very definitely the close relationship between the clay fraction of mineral soils and the phenomena of base exchange, adsorption and soil acidity. Treatment of acid soils with neutral salts results in many cases in the disappearance (adsorption) of some part of the added basic ions and the development of further acidity in the solution. The latter is attributed by many workers to the hydrolytic acidity of aluminium salts which appear in the solution. This may be ascribed to the result of a base exchange action, or to the solvent action of the soil complex of the acid; liberated through the adsorption of basic ions from the neutral salt.

The known toxicity of aluminium salts and the fact that this can be corrected by treatment with lime and with phosphates in water cultures as in the soil (Mirasol, *Soil Sci.*, 1920, **10**, 153 ;

Hartwell and Pember, *Soil Sci.*, 1918, **6**, 259) led to the fairly widespread acceptance of the theory that the toxic factor in acid soils was aluminium. Closer investigation of the soil conditions from the point of view of hydrogen-ion concentrations reveals certain points which make it difficult to reconcile this theory with actual facts. The work of Britton on the electrometric titration of aluminium salt solutions with lime and with silicates (see Chapters XV. and XVI.) indicates that equilibria included in the quaternary system $CaO—Al_2O_3—SiO_2—H_2O$ are most likely to control the solubility of aluminium salts in soil. The precipitation of aluminium hydroxide by lime begins at pH 4·2 and by silicate at 4·0 to 4·1. Moreover, in the lime titrations the redissolution of aluminium as calcium aluminate does not commence in solutions with lower pH values than 8 to 10. It is to be concluded, therefore, that in soils of pH values 4·0 to 8·0 little or no aluminium can be present in the dissolved state. Magistad brings forward data (*Soil Sci.*, 1925, **20,** 181) showing the improbability of the existence of more than 3 p.p.m. of soluble aluminium in soils of pH values 4·7 to 8·0. These contentions are largely supported by the analyses of displaced soil solutions by Pollard and his co-workers at the Imperial College of Science, London. No appreciable amounts of aluminium were found in soil solutions of pH 4·0 on the acid side ; and on limed soils, pH values of 7·5 to 8·0 were reached before aluminium again appeared in the soil solutions. On recently limed soils of *circa* pH 9·0 approximately 30 p.p.m. of aluminium were detected in the soil solution. These facts coupled with a number of American investigations in plant culture and field work tend to throw doubt on the belief in the toxicity of aluminium in acid soils.

From time to time suggestions have been advanced as to the existence of active alumino-silicic acids in soils which by reason of their nature might well be concerned in controlling soil reaction. They have also been regarded as amphoteric bodies existing in a state of combination which results from a form of dynamic equilibrium with dissolved ions in the soil (Loew, *Porto Rico Expt Sta. Bull.* 13, 1913). More recently, the tendency to identify alumino-silicic acids with the active substance in soil clay has been more pronounced. There is a tendency nowadays to regard the work of Bradfield (*Missouri Agr. Exp. Sta. Research Bull.*, No. 60, 1923 ; *J. Amer. Chem. Soc.*, 1923, **45,** 2669) as consolidating this view. He concluded from a comparison of the properties of soil colloids, separated from clay, with those of a mixture of hydrated silica, alumina, and ferric oxide, that the colloidal material consisted either of a definite compound or of a mixture of

compounds in which the oxides were chemically bound as alumino-silicates. The type of titration curve obtained with the hydrogen electrode when a solution of calcium hydroxide was titrated with a clay suspension was considered to be that of a weak acid, and he was therefore led to believe that the colloidal material in the soil was itself the acid. Saint (*Trans. 2nd Comm. Internat. Soc. Soil Sci.*, Gröningen, 1926, 134) has suggested that if a soil be represented as a partly neutralised acid, the amounts of different bases which any particular soil can absorb should be in equivalent proportions, and has advanced evidence to support the view in the case of the alkalis and the alkaline earths when considered separately, the difference between the two sets of figures being attributed to the formation of insoluble alkaline-earth salts. This, however, would be expected from a consideration of the very similar reactions which the alkaline earths and the alkalis enter into with hydrated silica.

The reaction involving the formation of the aluminium silicate precipitate affords no evidence of the existence of a complex aluminosilicic acid (Fig. 72). It is true that if the changes in hydrogen-ion concentration are followed when such a precipitate is subjected to treatment with solutions of alkalis or alkaline earths, the precipitate exerts a pronounced buffer action, which *primâ facie* might be regarded as indicating that the precipitate was an acid. This buffer action is, however, the result of the super-position of several reactions, *viz.*, (*a*) the reaction between the aluminium hydroxide and the base to form a soluble aluminate, buffering between pH 8 and 10 ; (*b*) the reaction between the base and the hydrated silica, giving rise to a gradual rise in pH from 6 upwards ; and (*c*) an equilibrium between the silicic acid and any soluble aluminate, *e.g.*, $Ca(AlO_2)_2$, which may have been initially formed, to give calcium silicate, $CaO,xSiO_2,yH_2O$, and hydrated alumina, producing a hydrogen-ion concentration from pH 6 upwards. The amount of soluble aluminate actually formed is doubtless a function of the amount of water present. Similarly, if the inorganic colloids of the soil be considered mainly as mixtures of hydrated alumina and silica, then the effect on the hydrogen-ion concentration of adding slaked lime to the soil would be determined by the reactivity of the two constituents with the lime. The titration curves of soil suspensions as obtained by Hissink and van der Spek (*Trans. 2nd Comm. Internat. Soc. Soil Sci.*, Gröningen, 1926, 72) with the hydrogen electrode all show buffer action between pH 6 and 8.

Whichever view may be accepted it is clear that any question of the physical adsorption of basic ions by clay may, to a great

extent, be discarded, and the reactions between soil and dissolved salts may be regarded as chemical processes.

The conceptions, however, of Gedroiz in Russia and by Hissink in Holland as to the nature of soil acidity and the related phenomena of base exchange and " adsorption " are built some-what on the lines of the presence of alumino-silicic acid in the soil. Briefly, the clay particle is regarded as consisting of an alumino-silicic acid substance presenting an outer layer of colloidal gel as its active surface and in which most of its chemical reactions are localised. Hissink regards this outer layer as the seat of an electrical double layer on the internal side of which are concentrated negative alumino-silicic ions, and on the outer side the positive ions of the soil bases (Ca, Mg, Na, K) and of hydrogen. These latter ions are concerned in base-exchange phenomena. The relative proportions of the individual ions are dependent on local soil conditions and are represented as being in equilibrium with the ions dissolved in the soil water which surrounds the clay particle. Soil conditions conducive to a high concentration of a particular ion in the soil solution bring resulting interchanges among the ions of the electrical double layer and an increase in the proportion of the particular ion therein. Thus the addition of (say) potassium chloride to a soil results in an increase in the proportion of potassium ions in the clay system and the appearance of an equivalent proportion of calcium and other ions in the soil solution. Moreover, by repeated leaching of a soil with potassium chloride solutions it is possible step by step to replace practically the whole of the basic ions of the clay by potassium ions and to obtain what is described as a " potassium soil." This process is of course reversible, and we must assume the existence of " calcium soils," " sodium soils," etc., characterised largely by differences in physical properties. It is not to be supposed that the relative proportions of basic ions in solution and those in the clay complex are directly proportional. On the contrary, the ease of displacement of one ion by another varies considerably. Thus a definite ionic concentration of $K^{\cdot}$ in the soil water produces a much greater dis-placement of calcium-ions from the clay than would a similar ionic concentration of $Na^{\cdot}$. The ease of displacement of the common ions would appear to be in the order, $Ca > Na > NH_4 > K > H$.

On the basis of the complex alumino-silicic acid hypothesis, it is to be assumed that acidity of the clay particle as a whole will depend on the relative proportions of base and hydrogen-ions which in turn is in equilibrium with base and hydrogen-ions dis-solved in the soil water. That this equilibrium is not a simple one is shown by the fact that the same relative change in pH

value of the soil extract does not produce proportionally similar changes in the base : hydrogen ratio as determined by Hissink (see later). These observations harmonize better with the view that the soil colloids are simply mixtures of hydrated alumina and silica. Below pH 7 there is a distinct tendency for the aluminum hydroxide to retain varying quantities of acids as basic salts, which on treatment with bases will undergo decomposition. Above the neutral point, bases react with both components forming both insoluble and soluble silicates and possibly aluminate.

The curves given in Fig. 72 also account for the presence of various metals in soil solutions of different pH values. As already stated aluminium is only found in a soil solution whose pH value is either less than about pH 4 or greater than pH 8. Many chemists have also found alumina in the neutral-salt extracts of sour soils ; thus, by the use of potassium chloride or nitrate, sodium chloride, etc., Veitch (*J. Amer. Chem. Soc.*, 1904, **26,** 637) concluded that the addition of sodium chloride to a soil did not liberate hydrochloric acid as such but aluminium chloride, and therefore the acidity was only apparent. Knight's (*Ind. Eng. Chem.*, 1920, **12,** 343) analysis of a soil extract with potassium nitrate shows that 90 per cent. of the titratable acid was in combination with alumina. Rice (*J. Physical Chem.*, 1916, **20,** 214) found aluminium in potassium nitrate extracts of which the pH's ranged from 3·5 to 4·5. Niklas and Hock (*Z. angew. Chem.*, 1925, **38,** 195) titrated potassium chloride extracts of soils with sodium hydroxide, using the hydrogen electrode. The first branch of their curve, corresponding to the decomposition of the aluminium salt, lies at about pH 4 (compare Fig. 62), and the remaining section shows a buffer action up to just above pH 8. The acidity of the more acidic soils is due to the normal hydrolysis of the aluminium salts formed in the soil.

The pH of soil solutions from sour soils after treatment with neutral salts often becomes still lower ; thus Crowther (*J. Agric. Sci.*, 1925, **15,** 212) found that soils of pH 4·78 on treatment with neutral salts gave about pH 4. Soils of $pH > 6$ appear to be unaffected by neutral salts, and their titratable or " mineral " acidity becomes negligible (compare Christensen and Jensen, *Trans. 2nd Comm. Internat. Soc. Soil. Sci.*, Gröningen, 1926, 111). The mineral acidity given by acid soils appears to depend on the extent to which neutral salts, when allowed to react upon soils, are able to cause an increase in hydrogen-ion concentration above that requisite for the precipitation of aluminium hydroxide, and thereby to enable alumina to pass into solution as a salt. The fact that the hydrogen-ion concentrations of such soil solutions are nearly

the same as that at which aluminium hydroxide is normally pre-
cipitated suggests that the soil must contain some aluminium
hydroxide in a partly neutralised state (*vide* p. 259). This would,
on hydrolysis through contact with water, give a *p*H near that
at which aluminium hydroxide becomes precipitable. When a
neutral-salt solution is added to such a soil, it is probable that the
salt splits up, the basic part combining with the preponderance of
silicic acid and being retained by the soil, and the acidic part
combining with the partly neutralised aluminium hydroxide to
enable some aluminium salt to pass into solution. Thus sodium
chloride might be considered to split up into sodium oxide and
hydrochloric acid, the sodium oxide attaching itself to the large
excess of colloidal silica and thus becoming insoluble, whereas
the hydrochloric acid, in reacting with the aluminium hydroxide,
causes some aluminium chloride to pass into solution and thereby
increases the hydrogen-ion concentration and the titratable
acidity. It is significant that this " exchange " acidity disappears
almost completely from soils of *p*H 6 and above. It is at this
point that aluminium hydroxide acquires its optimum insolubility,
due to the withdrawal of the small amount of acid radical which
it retained on being precipitated. Above this point, it behaves as
an acid and consequently is without effect on neutral salts.

Manganese has been found in solutions from certain acid soils.
Pollard (private communication) has found it in solutions of *p*H
up to 6 from certain sour soils. Rice (*loc. cit.*) found it in potas-
sium nitrate extracts up to *p*H 5 of acid soils. Fig. 72 shows that
the precipitation of manganese silicate does not begin until just
above *p*H 7. The *p*H of manganous salt solutions is of the order
5 to 6, but it must be remembered that, when a manganous salt
solution is treated with alkali in a quantity insufficient to start
precipitation, the solution rapidly decomposes through oxidation
and brown oxide separates. Hence it is unlikely that manganese
would be found in a soil solution of *p*H > 6.

Although ferric oxide is often a constituent of soils, very little
can pass into the soil solution, except in colloidal form, because
it is precipitated from strongly acid solutions (Britton, *J. Chem.
Soc.*, 1925, **127**, 2155). It can, however, sometimes be detected
in the neutral-salt extracts of sour soils by testing with an alcoholic
solution of potassium thiocyanate (Comber's test). Pollard (private
communication) found that by adding hydrochloric acid to soils,
the iron content of the aqueous extracts only became perceptible
when the solutions had become more acid than *p*H 1·5.

The phenomenon of base-exchange in soils has been attributed
by Raman to the existence of zeolitic combinations in the inorganic

colloidal matter, in spite of the fact that zeolites themselves do not occur in soils. As will be evident from p. 313, the active constituents of soils and zeolites are the same, to which in all probability the " base-exchange " exhibited by both must be attributed.

The question of the nature of the operative factor in acid soils which brings about plant injury is still not definitely answered. The presence of neither free mineral acid nor of aluminium salts can be satisfactorily substantiated experimentally. Are we to suppose the hydrogen-ion itself is a plant poison or indeed are the ill-effects on plant growth of acid soils really the effects of a poison in the true sense of that word ? To distinguish direct toxicity from injury through some secondary effect is a difficult matter. It has been suggested that in the absence of definitely poisonous materials in acid soils it may well be that conditions conducive to an excessive proportion of hydrogen-ions in the soil may also affect the proportions of other cations in a manner which militates against satisfactory plant nutrition. Obviously the plant growing in soil does not absorb and utilise the minerals in the soil solution in whatever proportions they occur. The present conception of the nutritive process as being akin to ionic transmission through the same permeable membranes of the root tissues, must include a recognition either of the mutual effect of the various ions on the rate of their diffusion, or of some internal mechanism of the plant giving some measure of control of the nature and proportion of the ions entering the root hairs. It is then conceivable that the presence of excessive proportions of hydrogen-ions or alternatively, of conditions producing them, may influence the diffusion of one or more of the mineral nutrients to an amount which induces malnutrition of the plant ? It is known, for example, that the phosphorus intake of plants is fairly sensitive to changes in pH of the nutrient medium, and also that the rate of absorption of certain cations by the root hairs increases with decreasing pH values of the nutrient.

Availability of Phosphorus.

The hydrogen-ion concentrations of soil solutions play an important rôle in rendering any phosphorus the soil may contain available to the plant. Britton (*Jour. Chem. Soc.*, 1927, 620) has calculated from the data of Bassett (*ibid.*, 1917, **111,** 624 ; *Z. anorg. Chem.*, 1908, **59,** 1) relating to the ternary system, $CaO—P_2O_5—H_2O$, that calcium phosphate, either the di- or tri-phosphate, is not precipitated from solutions which are more

acid than pH 5·5 (approx.). Addition of slaked lime converts the CaHPO$_4$, first precipitated into Ca$_3$(PO$_4$)$_2$ without any apparent change in pH, and this in turn may be rendered basic to an extent corresponding to 3Ca$_3$(PO$_4$)$_2$,Ca(OH)$_2$, called " hydroxyapatite " by Bassett, with a change in pH to 5·9. (See Chapter XVIII.)

The foregoing is of interest on account of its bearing on the reactions which take place in soils when treated with phosphatic fertilisers. If the pH of the " soil solution " falls below 5·5, the calcium phosphate in the soil will pass into the soluble state, though when in this condition there will be a great tendency for some of the phosphate to suffer " reversion " through reaction with colloidal alumina, but when lime is added so as to raise the pH to 5·5 and above, the phosphate begins to become insoluble, initially as the dicalcium salt, and finally as the basic phosphate. It is probable, as stated by Bassett, that " hydroxyapatite " is the phosphate which exists permanently in soils under ordinary conditions, for any di- or tri-calcium phosphate which may first be formed will ultimately become decomposed.

Soil solutions in equilibrium with the dicalcium phosphate contain relatively large amounts of partly neutralised phosphoric acid which, when removed, either by " reversion," or by the plant, or by drainage, will cause the solid phases to decompose and eventually to become basic without any great change in pH taking place. The conversion of the phosphate into the insoluble basic state renders it unavailable to the plant. Thus Gedroiz (*Zhur. Opit. Agron.*, 1911, **12**, 529) found that tri-calcium phosphate gave the best immediate results on soils not saturated with bases. The necessity of having the soil just on the acidic side of neutrality has recently been emphasised by von Wrangell (*Landw. Vers.-Stat.*, 1920, **96**, 1), who recommends the use of " physiologically acid fertilisers," such as ammonium sulphate, to render any phosphate available.

The ease with which aluminium phosphate becomes decomposed on decreasing the hydrogen-ion concentration, even though the reagent used may itself be a soluble phosphate, throws some light on the manner in which vegetation obtains its phosphorus from the soil. When a soluble phosphatic fertiliser, such as superphosphate of lime, is added to a soil, and especially if the soil be sour, " reversion " of the phosphate occurs through the formation of insoluble phosphate on the surfaces of the colloidal particles of hydrated alumina and ferric oxide (see, *e.g.*, Lichtenwalner, Flenner, and Gordon, *Soil Sci.*, 1923, **15**, 157 ; Hall and Vogel, *ibid.*, p. 367). Marais (*ibid.*, 1922, **13**, 355), in a study of the application of aluminium phosphate as a fertiliser, concluded that,

in spite of its low solubility in citric acid, it is of service in soils well stocked with lime, but should never be used on acid soils unless lime is applied in intimate contact with it. Slaked lime causes aluminium phosphate to decompose with the formation of soluble calcium phosphate until pH 5·5 is reached.

The soils of Assam used for the production of tea and indigo are rich in available phosphate. According to W. R. G. Atkins, Assam soil has a pH of 5·4, which thus explains the availability. The acidity was due to the oxidation of sulphur originating from the iron pyrites contained in the soil. The development of acidity in soil may be induced by treatment with sulphur, which may undergo not only direct oxidation but oxidation promoted by sulphur bacteria. It is not surprising therefore to find that soluble phosphate manures have been prepared by composting sulphur and phosphatic manure.

Thus although the available evidence as to the process whereby acid conditions induce plant injury is by no means conclusive, the correlation of pH in the soil and plant growth is very definite. Determinations of hydrogen-ion concentration, therefore, must have very considerable value in the elucidation of what is now being recognised as an agricultural problem of widespread importance.

Determination of the Lime Requirement of Soils.

The development of ideas as to the cause and effect of sourness in soils is reflected in the methods which have from time to time been adopted for its measurement. This has resolved itself into the more practical process of measuring the amount of lime necessary to counteract this fault—the lime requirement. Earlier methods were simple and direct but empirical. In a general practical way soils which contained no carbonates as shown by effervescence with acid were deemed to need lime. More ac- curate measurements of a quantitative nature involved the deter- mination of the amount of lime which the soil could absorb (*e.g.*; Veitch, *J. Amer. Chem. Soc.*, 1902, **24**, 1120) or of the quantity of carbonate or bicarbonate of calcium which the soil reacted with as measured by the evolution of carbon dioxide (Hutchinson and MacLennan, *J. Agric. Sci.*, 1915, **2**, 25 ; MacIntyre, *J. Assoc. Off. Agric. Chem.*, 1915, 417 ; and Knight, *Ind. Eng. Chem.*, 1920, **12**, 340, 457, and 559). These methods have had very consider- able value, more particularly in recent years when the cost of trans- port and distribution of lime has assumed greater relative import- ance. From a scientific standpoint such methods leave much to be desired. The equilibrium between soil—CaO—CO_2—$CaCO_3$

has been shown to be sensitive to changes of external conditions (Crowther, *J. Agric. Sci.*, 1925, 201 *et seq.*), and it is evident that the wide discrepancies between the various methods (Fisher, *J. Agric. Sci.*, 1921, **11,** 19) are in part due to this fact and partly to the different processes not all leading to the measurement of the same basal reaction. As a result, a comparison of the lime requirement of different soils by the same process and of the same soil by different processes is impossible. The best value can only be obtained in this way, if used in conjunction with soil survey maps by workers of experience.

The base-exchange theory of soil acidity is illustrated by lime-requirement methods of Hopkins (*U.S. Dept. Agri. Bur. Chem. Bull.*, 73 (1903)) ; Jones (*J. Assoc. Off. Agric. Chem.*, 1915, **1,** 43) ; and Darkühara (*Bull. Imp. Cent. Agric. Exp. Sta. Japan*, 1914, **2,** 1), in all of which the acidity developed by treating soil with solutions of salts is measured, and later by Comber who measures acidity by the ferric thiocyanate coloration produced by the liberation of iron from acid soils by neutral salt treatment.

A number of indirect methods for measuring the hydrogen-ion concentration of soils has been advanced, *e.g.*, those involving the inversion of cane sugar, the hydrolysis of esters and the decomposition of iodide-iodate solutions (Baumann and Gully, *Exp. Sta. Record*, 1908, **19,** 1008).

Later came the refinement of the technique in the direct determination of pH values, and the many attempts to correlate pH and lime requirement. The definite association of " sourness " and " acidity " had persisted throughout years of investigation and much enlightenment was expected from research in which actual hydrogen-ion concentrations could be accurately measured. Practical measurements of pH values in soils are made either by the colorimetric methods of Clark and Lubs (*J. Bact.*, 1917, **2,** 1, 109, 191), or the simplified method of Gillespie (*Soil Sci.*, 1918, **6,** 219), or preferably where accuracy is more important, by direct electrometric methods using a hydrogen or quinhydrone electrode. The last named process is that devised and adapted for soil measurements by Biilman (*J. Agric. Sci.*, 1924, **14,** 232 ; see also Biilman and Jensen, *Trans. 2nd Comm. Internat. Soc. Soil Sci.*, B., 1927, 236). It is more rapidly performed than with types of apparatus utilising hydrogen electrodes, and except for its limitation on the alkaline side of pH 8·0 is as satisfactory. Probably the best hydrogen-electrode apparatus for the purpose is that devised by Crowther (*J. Agric. Sci.*, 1925, 15) and illustrated here.
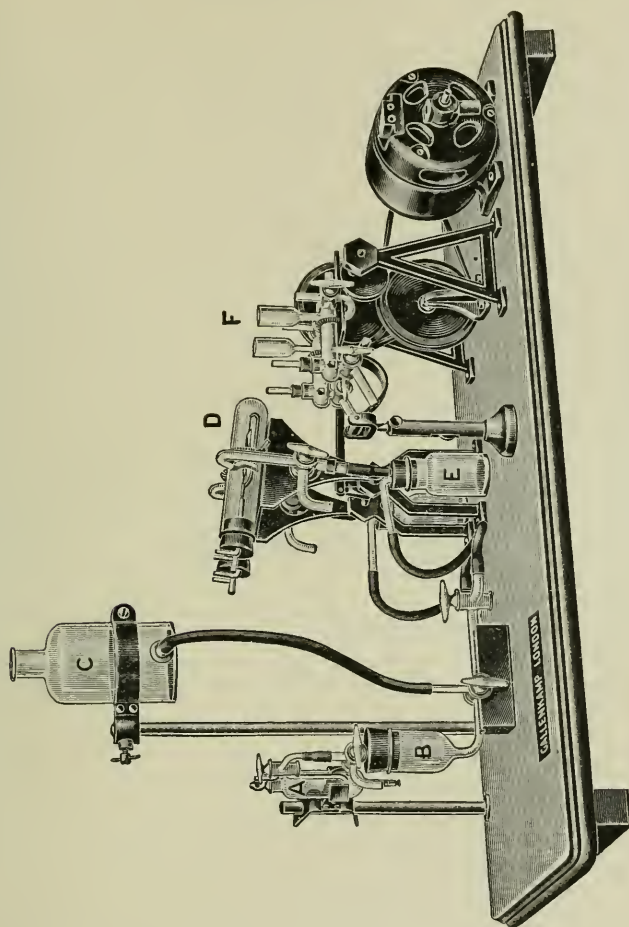
FIG. 104.—Crowther's Apparatus.

The special features of the apparatus are :—

(1) The electrode vessel (D) and the platinum electrode are both large and continuously rocked so as to secure rapid equilibrium between the hydrogen and the soil suspension.

(2) The junction between the soil suspensions and the saturated potassium chloride connecting solution is made below a three-way tap in a bent syphon tube. In this way the entrance of potassium chloride into the electrode vessel is prevented and a wide well-mixed liquid junction is obtained. Any soil flocculated below the three-way tap is caught in special traps (E).

(3) The reservoir (B) provides for the use of both a saturated calomel electrode and a standard N/10 calomel electrode (A), the latter being provided with the Koehler device for preventing diffusion from the saturated potassium chloride solution.

(4) Two determinations may be made simultaneously.

(This particular apparatus as supplied by Messrs. Gallenkamp contains a Clark's rocking hydrogen electrode shown as F; see Fig. 6.) Whilst the apparatus adopted for hydrogen-ion measurements is now of a high order of excellence, details of technique have hardly reached a satisfactory standard. A considerable amount of discussion has arisen from time to time as to the manner in which the soil sample should be prepared for pH determinations.

No satisfactory means are available for measurements in the soil *in situ*—obviously the ideal method—and we are limited to the examination of soil extracts, on the manner of preparation of which much depends. If water extracts are made, the question of the proportion of soil to water used is important. Crowther has recommended a ratio of 1 : 5 for the purpose, but in very many cases a narrower ratio of 1 : 2·5 or 2·0 is adopted in the belief that a fairer representation of the true value is thus obtained. On the assumption that there exists in soil an equilibrium between the dissolved cations and those intimately associated with the clay particles but not in true solution, there is to be considered the possibility of a disturbance of this equilibrium following the addition of water to the soil, and the pH value of the extract may differ from that of the natural soil. The extent of the displacement of the equilibrium depends largely on the nature of the soil itself and the ratio of soil : water used. A moderate ratio (up to 1 : 5) does not markedly affect the observed values of most soils of pH values 6 to 7, but tends to give low values on the acid side and high values on the alkaline side of this range. Wide ratios of soil : water usually tend to yield observed values nearer to the neutral point than those found when small proportions of water are used. The proportion of carbon dioxide in soil influences the results obtained in wide ratio extracts to a marked extent.

R. H. Bray (*Ind. Eng. Chem.*, 1928, **20**, 421) has devised a simple form of hydrogen electrode vessel, shown in Fig. 105, in which he measures the hydrogen-ion concentration of soil suspensions that are kept in a state of constant agitation by the passage of hydrogen. To carry out a measurement 10 grams of soil are

mixed with 25 c.c. of distilled water, and after the gas has been
passed for 13 minutes the salt-bridge is connected and a reading
taken, and then another 2 minutes later. He emphasises the fact
that the pH of the supernatant liquid will be somewhat different
from that obtained before the soil particles are allowed to settle.
A difficulty encountered, however, is that the moving particles
tend to wear the electrodes bright.

Again there arises the question as to whether the soil extract
should be filtered, or centrifuged or whether the actual soil sus-
pension may be used.
Filtering has been dis-
credited owing to ob-
served alterations in the
pH value of the extract
during passage through
the filter paper, and
similar though smaller
changes are recorded
when the suspension is
centrifuged. In some
cases these differences
are large, *e.g.*, the
values for a number
of soils examined by
means of suspensions
were in the range pH
4·1 to 5·0, but when
the suspensions were
filtered or centrifuged
the range of observed
values rose to 6·2 to
7·4. These discrep-

FIG. 105.—Bray's Form of Hydrogen Electrode
Vessel.

ancies are largely reduced by thoroughly shaking the soil suspen-
sion. It is suggested by way of explanation that the colloidal
coatings of the soil particles of the surface exposed on a filter
paper or centrifuge tube to the aqueous extract, may act as a
semi-permeable membrane and allow unequal diffusion between
the soil mass and the extract, thus causing alterations in the
hydrogen-ion concentration of the latter. Shaking, by disrupting
this membrane, leads to the maintenance of a more steady value in
the extract. It has been observed that similar changes in pH
values occur in dilute salt solutions exposed to gelatinous alu-
minium and ferric hydroxides.

Some investigators prefer to substitute a neutral salt extract

for a pure water extract in pH determinations specifically designed
for the calculation of lime requirements as bringing into effect
the exchange acidity of Kappen (*Z. Pflanz. Düng.*, 1924, 3A, 209).
From this point of view the method may have certain advantages,
but it would seem preferable to adopt the simple water extract
as giving results approaching more closely the actual pH value of
the natural soil.

For the practical purpose of determining lime requirements
some connexion has been sought between the existing soil reaction
and the amount of lime required to bring this to neutrality. Both
theory and observation pronounce this impossible. All soils
have considerable but widely differing buffer capacities, *i.e.*, they
contain active material tending to counteract changes in reaction
brought about by the addition of basic or acid substances. Apart
from the small amounts of dissolved buffering salts (phosphates,
carbonates, salts of organic acids, etc.) and possible reserves of
calcium carbonate, both the clay and the humus act as buffering
agents with considerable effect. The known variation in the pro-
portions of the latter in various soils is sufficient to preclude any
possible relationship between the existing pH value of an acid
soil and its lime requirement. The *modus operandi* of any deter-
mination of lime requirement based on hydrogen-ion measure-
ments must be in the nature of an electrometric titration to a
definite pH value.

No standardised practice has as yet been adopted. Apart from
variations in observed pH values brought about by modifications
in technique above referred to, there are additional debatable points
as to correct procedure. A strict comparison between laboratory
and field liming operations introduces obvious difficulties in the
matter of the distribution of lime in the soil in the laboratory
and the control of its reaction with soil in the field under similar
conditions. To titrate a soil suspension with lime introduces
the possible error due to the use of soil : water ratios which are
never obtained in the field, and in addition the reaction end-point
would probably not be the same in both cases. Similar but un-
controllable errors may intervene if extracts of soil treated with
dry lime, as in the field, are examined. In the latter case, too, the
time of reaction is prolonged to varying extents in different soils
and some kind of arbitrary standard is demanded. Satisfactory
measurements can be made, by a standardised laboratory tech-
nique yielding data, from which the amount of lime required
in the field can be calculated. Christensen and Jensen have
elaborated a method (*Trans. 2nd Comm. Internat. Soc. Soil Sci.*,
1926, A., 94) whereby the soil is titrated with lime water to a

*p*H value of 7. The amount of lime so needed multiplied by 3 (the " liming factor ") gives a reasonably close approximation of the true lime requirement. The " liming factor "— obtained by purely empirical means is doubtless accounted for by the less even distribution of lime in the field and its less rapid reaction with the soil, combined with losses of lime by drainage to subsoil, etc., during the reaction period. Before leaving the matter of electrometric soil titrations, reference should be made to another valuable measurement—the " buffer capacity " of soil. This value is represented by Jensen (*Intern. Mitt. Bodenk*, 1924, **14**, 112) in the form of a graphical surface area. The *p*H values of a number of soil samples treated with increasing amounts of acid and alkali are determined. The curves interpreting the results are of the form shown in Fig. 106.

The area lying between this titration curve and the base curve of a buffer-free soil is the buffer capacity. The buffer capacity represents the ability of the soil to withstand changes of reaction and gives expression in a concrete form to the possibility of a soil becoming acid in the near future or alternatively some conception of the period for which a given lime treatment is likely to suffice.
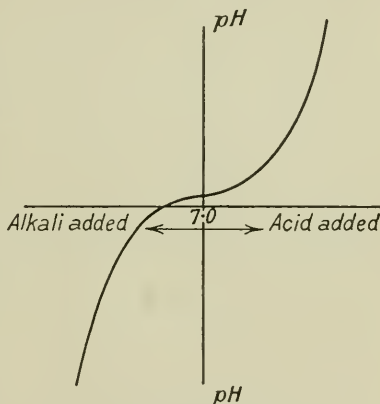
FIG. 106.—Buffer Curve of Soil.

Brief reference should be made here to the methods of Hissink and Gedroiz for determining lime requirements although actual measurements of hydrogen-ion concentrations are not involved. The method is based on a consideration of the clay (or humus) particle and its surrounding double ionic layer described previously. The clay particle carrying a definite charge is associated with a definite equivalent of cations in the outer shell. The total base equivalent with which the clay can combine is designated " T," the amount of a particular base ion present as " S." The condition of the clay particle is represented as the degree of saturation " V " where $V = 100\frac{S}{T}$. This is to be considered as the percentage of the maximum possible base ions which are actually present under the conditions of experiment. Smaller values of V correspond with smaller amounts of basic ion present and there-

fore with larger proportions of hydrogen-ions in the clay complex and hence greater acidity. Experimentally the calcium values are measured. The value " S " is obtained by prolonged leaching with ammonium chloride, and a determination of the calcium so removed. T—S is obtained by titration with free base to complete saturation. From these figures the value " V " is calculated. It is calculated that V for neutral soil is approximately 55 per cent. Hissink has shown general relationships to exist between the values V, S, and the pH value and calculates his lime requirement as that required to produce pH 7·0. The general application, however, of these values to all soils leads to some conflict of opinion (cf. Sigmund, Proc. 2nd Comm. Internat. Soc. Soil Sci., 1926, A. 55).

From the foregoing it is clear that in the general problems of plant nutrition and of microbiological activities in the soil and within the plant tissue, the reaction of soil and plant sap is of vital importance. Data obtained have already enabled great advances to be made in this sphere and continued investigation must inevitably enhance our knowledge of the vital processes. In the study of soil chemistry in general and of the problem of sourness in particular, much has been gained from the investigations of the causes and effects of changes in hydrogen-ion concentration, the importance of which as a factor in the chemical evaluation of soil fertility is now generally recognised.

CHAPTER XXXI.

HYDROGEN-ION CONCENTRATIONS AND CERAMICS.

EXCEPT for small amounts of oxides of iron, titanium, calcium, and the alkali metals, clay comprises mainly hydrated alumina and silica. Though its composition is not by any means constant, those varieties which are suitable in the ceramic industry correspond to formulæ ranging in silica-content from $Al_2O_3,1\cdot5SiO_2,$ $2H_2O$ to $Al_2O_3,3SiO_2,2H_2O$. The ideal clay is usually considered to have the composition shown by the formula of kaolin, $Al_2O_3,2SiO_2,2H_2O$. Clay is probably more than a simple mixture of two colloidal hydrated oxides, for there is good reason to believe that chemical forces, though certainly very weak, exist between some of the weakly basic alumina and some of the weakly acidic silica. Thus we saw on page 307 that the precipitate obtained by adding a dilute " water-glass " solution to one of aluminium sulphate is a basic aluminium silicate, which begins to separate from solution at $pH\,4$. It is surprising that the precipitate should have been basic, in view of the fact that the sodium silicate solution used contained a large proportion of silica. Schwarz and Brenner (*Ber.*, 1923, **56**, B., 1433) also found that the precipitates obtained with sodium silicate from aluminium chloride solutions contained silica in amounts slightly greater than required by $Al_2O_3,1\cdot5SiO_2$. Using a great excess of reagent the dried precipitate approximated to $Al_2O_3,2SiO_2,2H_2O$. This precipitate, however, differed from kaolin in that it was decomposed by concentrated hydrochloric acid with comparative ease. Though the samples were shown by means of X-ray spectrographs to be amorphous after ageing for periods up to 8 days, it was observed that thereafter they began to assume a crystalline structure similar to that of kaolin. In ordinary clay the effects of ageing become very marked, as may be seen from their enhanced resistance to attack by concentrated solutions of acids and alkalis. Nevertheless, clay may be acted upon by acids and alkalis, though with dilute solutions the reactions which occur can hardly be described as other than incipient. Small as they are, the addition of reactants in small concentrations to clay suspensions, which vary the hydrogen-ion

concentration, results in appreciable physical changes in the colloidal solutions.

Clay is composed of fine-grained particles whose surfaces have become more easily attackable through the action of water and weather. These fine particles are thus covered with a film of colloidal aluminium hydroxide and silicic acid, and it is the reactions into which they can enter with the various flocculating and deflocculating agents that determine the properties of " clay-slips " and of clay. The various stages of the reactions involving these substances are controlled by the hydrogen-ion concentrations which the reagents are capable of setting up. It is therefore
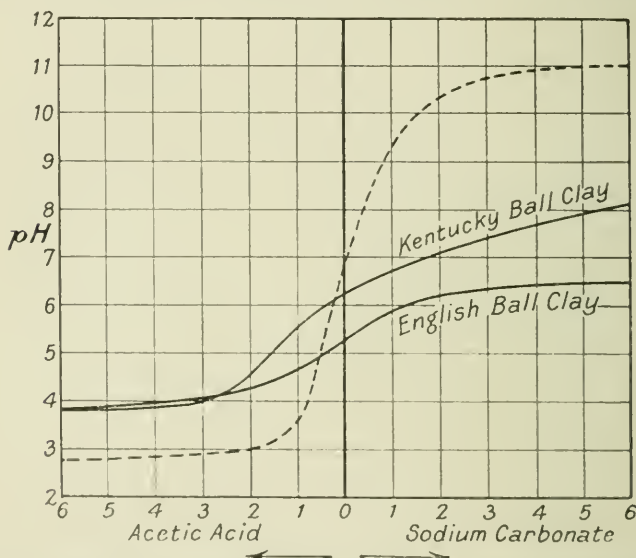
FIG. 107.—pH of Water-Clay Extracts on Treatment with (1) Acetic Acid, (2) Sodium Carbonate.

probable that pH measurements will assume greater importance in pottery work, though it must be conceded that the results of the few workers who have interested themselves in this problem sometimes appear to be conflicting.

An idea of the nature of the reactions of clay with acids and alkalis may be obtained from Fig. 107, in which are shown the variations in pH of water-clay extracts, 12 : 1, caused by the addition of acetic acid and sodium carbonate. The broken line shows the effect of adding these reagents to water alone. The curves were taken from a paper by Randolph and Donnenwirth (*Jour. Amer. Ceramic Soc.*, 1926, **9**, 544). The acid branches of

the curves refer to the interaction of the aluminium hydroxide gel with the acetic acid, and it is interesting to note that throughout the major part of the reaction the pH was about 4. Such a value would be expected, for the aluminium salt formed must have been in equilibrium with an excess of undissolved aluminium hydroxide, and thus the conditions were not very different from those ruling for the reverse reaction, $viz.$, that of precipitation. Considerable action occurred between the clay and the sodium carbonate, as shown by the position of the titration curves compared with the broken-line curve. The buffered curves show that equilibria must have been set up between the silica and the hydrolysed sodium hydroxide, though the low pH values indicated were probably the result of the action of some acid which the clay originally contained in combination with the alumina gel. The fact that clay on treatment with water gives rise to extracts whose pH values generally lie between 4 and 5 (Hall, *J. Amer. Cer. Soc.*, 1923, **6**, 991) suggests that the dissolved portions must be soluble basic aluminium salts (compare page 260), and as the solutions thereby obtained are colloidal, it appears that some kind of equilibrium must exist between the colloidal particles and the solutes. We might therefore regard particles of clay as being made of more or less insoluble nuclei of differing grain size surrounded by a colloidal film containing silica, alumina, some basic aluminium salt and water. On coming into contact with water some of this basic aluminium salt passes into solution, establishes an ionic equilibrium between the liquid and solid phases in which micellar ions of clay particles play a considerable part tending to stabilise the colloidal solution. Clays of alkaline reaction probably contain no basic salt but instead contain some silica in combination with alkali or alkaline earth in a soluble condition. According to Hall's data aqueous clay extracts may have pH values ranging from 3 to 8·4. The hypothesis here advanced accounts for Hall's observation that in general a clay which gives an acid extract with the first addition of water will decrease in acidity as successive amounts of water are added, and that clays giving an alkaline extract usually decrease in alkalinity on washing.

Plastic clay is, of course, clay in the flocculated condition. The degree of plasticity of a clay is the factor on which many of the desired properties of the finished article seem to depend. Plasticity refers to the effect of pressure applied to clay and the deformation which is thereby effected. It may be that the cohesive forces, which exist between the clay particles, are involved in the question of the amount by which clay can suffer alteration in shape without falling apart. The forces of cohesion only come into

play when the particles are sufficiently close to one another, and it is in this regard that the size and nature of the colloidal film and also the size of the insoluble clay particles become of importance. Hydrogen-ion concentration may prove to be an effective factor in the control of these surface films. Various methods have been adopted to secure control of the plasticity of clays, based on the power of the colloidal matter to absorb various salts and dyes and also on the viscosity of the clay-slips. If water is added to clay it becomes increasingly plastic, until an amount is added which results in stickiness. Thereafter, more water produces a clay suspension, known as the clay-slip.

Where articles are manufactured by casting, the production of efficient clay-slips becomes a matter of vital importance. Thus according to Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. VI., 489, a clay-slip prepared with about 0·3 per cent. of a mixture of sodium carbonate and silicate can be readily poured in casting operations, though it may contain less water than a stiff mass of clay which has not been treated with alkaline solution. On adding a little acid to the clay-slip in an amount sufficient to neutralise the alkali it contains immediate " solidification " ensues, so that the vessel can be inverted without spilling the contents. If more alkali be now added the clay assumes its former fluid condition, though the amount of alkali mixture to be added varies from clay to clay. Randolph and Donnenwirth (*loc. cit.*) state that the addition of small amounts of acid or alkali affects the viscosity of the clay-slip and the way in which it acts in the casting mould, so influencing the plasticity and strength of the dry clay. Electrolytes present in the clay often have an effect on the strength of the clay pieces in the dry state. The viscosity—pH relationship differs from clay to clay, but nevertheless it may prove to be of considerable use in connexion with the particular batches of clay for which they may be determined. Due to the complex physical nature of clay it is likely that pH data will have to be considered in conjunction with other properties, *e.g.*, rate of settling, soluble matter, contraction and strengths in the dried and fired conditions when fired at different temperatures. Fessler and Kraner (*J. Amer. Cer. Soc.*, 1927, **10**, 505) could, however, find no relationship between pH data and viscosity or other properties. Randolph and Donnenwirth concluded that there was a relationship between the pH of the slip and the breaking strength of the finished clay-ware ; they found that the maximum strength occurred in those products prepared from slips at pH 6, irrespective of the acids used.

The rate of settling of a clay suspension is a function of the

pH of the medium, in that it affects viscosity by promoting the dissolution of colloidal matter at certain pH ranges. At pH values below 4 aluminium hydroxide passes into true solution and at values higher than about pH 9 slow dissolution of the silica occurs, though it does not become considerable until an alkalinity of the order of pH 12 has been acquired. Hall (*J. Amer. Cer. Soc.*, 1923, **6**, 991) found that the maximum rate of settling lies between pH 2·7 and 4·0 (see also Olof Arrhenius, *J. Amer. Chem. Soc.*, 1922, **44**, 521). As this range lies immediately below the aluminium hydroxide precipitation pH, it appears that the settling out of the particles must be due to the partial removal of the colloidal layers from the surfaces of the clay particles in forming a less viscous solution. He found that the range for maximum deflocculation (*i.e.*, peptisation) was pH 10 to 12 which was caused by a steady reaction of the alkalis with the clay. This action may be accounted for by the formation of clay micellar anions, through the initial adsorption of the alkali and the subsequent partial dissolution and ionisation of some of the sodium clay complex.

The pH of clay-slips which are to be used for casting lies between 5·5 and 9·3. For the manufacture of goods not necessitating the use of pure clays the most suitable pH will usually be found to lie in the lower half of this range. This applies to fire clays. For purer clays, *e.g.*, white clays, the optimum pH is higher, and lies somewhere above the neutral point.

As recommended by W. A. Taylor (*The A B C of Hydrogen Ion Control*, La Motte, 1928, p. 46), the water in which a clay body is suspended can usually be separated by filtration through an alundum filtering cup under air pressure applied above and around the cup. The clear solution thus obtained may be used for the colorimetric determination of pH.

CHAPTER XXXII.

THE TEXTILE AND DYE INDUSTRIES.

THOUGH the value of the control of hydrogen-ion concentration in textile processes is only just beginning to be realised, the investigations which have hitherto been carried out indicate that it is a matter of definite practical importance. This applies more particularly to the wet processing of the ampholytic substances, silk and wool, and especially to their dyeing.

Among other substances, acids and alkalis may have a particularly deleterious effect on the proteins of wool and silk by promoting their hydrolysis. Such damage, which is often difficult to detect, may render the fibres susceptible to attack by the chemicals in the later processes, and thereby impair the finished product as regards its tensile strength, elasticity, and wearing qualities. Though examination of the fibres under the microscope will reveal damage when it has advanced sufficiently far, it cannot be relied upon for the detection of an incipient attack. Thus the damage of wool fibres caused by acid begins on the epithelial scales, which through their consequent wrinkling are visible through the microscope as striations, whilst continued hydrolysis causes them to disintegrate, and finally to dissolve. The damage done by alkalis is more difficult to observe since their attack is initially localised on the cortex, which may be even dissolved out without any appreciable effect on the epithelial scales. It is therefore desirable to have a means by which the amounts of acid and alkali in wool fibres can be detected and estimated. King (*J. Soc. Dyers and Col.*, 1927, 321) has devised a method based upon the buffering effects which these impurities may have on the hydrogen-ion concentration of acetic acid, and the shade of colour assumed by the fibres when dyed with certain of the sulphonephthalein indicator dyestuffs. The dyeing is performed at room-temperature with a suitable indicator in a bath containing acetic acid equal in weight to 1 per cent. of the weight of the wool, after which the temperature is very slowly raised to the boiling-point.

Table 103 gives some idea of the percentage amounts of acid which can be estimated from the tints of the dyed wool.

TABLE 103.

PERCENTAGE OF ACID IN WOOL.

Indicator.	Colour Change with Increasing Concentration of Acid.	Percentage of Sulphuric Acid (on Dry Weight of Wool).
Thymol blue	Yellow-orange red-magenta red	4·5–7
Bromophenol blue	Blue-greenish blue-yellow	3–5
Lacmoid	Slate blue-puce red	1·5–3
Bromocresol purple	Purplish-dirty blue-yellow	0–2
Bromothymol blue.	Bluish-green-yellow	0–1

By using a range of indicators, comprising bromothymol blue, phenol red, cresol red, and thymol blue, it is possible to estimate the pH of wool from that of neutrality successively to that of 5 per cent. sodium carbonate. In general, acid dye-baths may have as high a hydrogen-ion concentration as pH 1·5 without incurring any serious harm. This, however, should be regarded as a limiting value. The extent of alkalinity varies with the different types of fabric. For example, cotton will stand solutions of pH up to 12 or 13 without any great risk ; in fact, alkaline solutions of such a pH value are used for the removal of impurities on account of their rapid action. Regarding the finishing of wool and silk, it is found that both too little and too great an alkalinity of the re-spective scouring and degumming baths lead to unsatisfactory results. For wool scouring, a soap solution containing sufficient soda to raise the pH to between 10 and 11 is used, though the temperature should not be allowed to go beyond 60° C. In the degumming of silk pH 10 is required.

The application of pH control to peroxide bleaching liquors has been investigated by Trotman and Trotman (*J. Soc. Dyers and Colourists*, 1926, **42**, 154). They found that the best bleaching, together with the least amount of structural change in the fibres, is obtained at pH about 10. Incidentally this pH is economical when the amount of bleaching agent is taken into consideration. The fact that in acid bleaching liquors, acetic acid, instead of a mineral acid, is used in conjunction with either sodium bisulphite or potassium permanganate emphasises the effect of the hydrogen-ion concentration. The presence of the acetic acid regulates the pH of the baths at about pH 3.

Most work appears to have been directed to dyeing operations, which, in the case of the protein bodies contained in wool and silk, involve mainly chemical combinations between acidic and

basic groupings. The quantity of an acid dye adsorbed by a protein appears from the work of Chapman, Greenberg, and Schmidt (*J. Biol. Chem.*, 1927, **72,** 707) to be proportional to the amounts of its basic components, *viz.*, arginine, histidine, lysine. They were unable to obtain any evidence of physical adsorption between pH 2·5 and 1·0. The dyeing of wool has been investigated by Briggs and Bull (*J. Physical Chem.*, 1922, **26,** 845), Reinmuth and Gordon (*Ind. Eng. Chem.*, 1923, **15,** 818), and quite recently by Elöd and Pieper (*Z. angew. Chem.*, 1928, **41,** 16). Wool at pH 2 takes up twice the amount of Crocein Orange as it does at pH 5, the isoelectric point being at pH 4·6. The behaviour of Crystal Violet when applied to wool in liquors of initial pH values ranging from pH 1 to 12 is typical of that of many basic dyes. The absorption steadily approaches a maximum value from a solution at pH 10. That enhanced dye-absorption should occur within the alkaline range is in accord with the functioning of the acidic groups of the protein molecule. A constant absorption of dye took place in the vicinity of the isoelectric point, from pH 4·07 to 5·75. Ultramicroscopic examination afforded an explanation of the unexpected maximum absorption at pH 10, in that it showed that the dye particles then underwent an appreciable increase in size, thereby impeding the dye penetration. Similarly the absorption of acid dyes decreases rapidly when the pH of the dye solution exceeds the isoelectric point. The fact that a basic dye is absorbed at all by wool or silk when they are behaving as bases, *i.e.*, at pH values less than pH 4·6, and that an acidic dye is taken up at higher pH values, when the acid nature is prevailing, may be due either to (*a*) the great insolubility· of dye (basic) — protein (acid) or dye (acid) — protein (basic) complexes, or to (*b*) physical adsorption. Substances used in " weighting " silk have marked effects upon the amounts of dye absorbed and the pH values which are conducive to the most efficient absorption.

The importance of hydrogen-ion concentration in the application of dyes to mordanted fabrics such as cotton will be apparent from Table 104 in which data are reproduced from a paper by Marker and Gordon (*Ind. Eng. Chem.*, 1923, **14,** 818) concerning the absorption of acidic and basic dyes by hydrated alumina.

It will be seen from page 260 that aluminium hydroxide behaves as a base below pH 4, and assumes the nature of an acid above pH 8. The table shows that while there occurred some absorption of methylene blue and crystal violet from the acid solutions which were below pH 4, the absorption became very pronounced with increasing pH values. Using the acidic dyes,

TABLE 104.

ABSORPTION OF ACIDIC AND BASIC DYES BY ALUMINA
(mg. Dye per 1 gram of Dry Gel).

Basic Dyes.				Acidic Dyes.			
Methylene Blue.		Crystal Violet.		Orange II.		Metanil Yellow.	
pH.	Mg.	pH.	Mg.	pH.	Mg.	pH.	Mg.
1·96	65·6	1·50	3	2·30	452	1·92	703
2·23	66·1	5·44	8	3·20	186	2·30	406
5·95	67·5	9·18	45	5·27	179	7·46	276
9·85	77·0	10·70	282	10·14	162	9·67	226
11·12	82·7	11·12	413	11·02	136	11·60	115
12·00	279·0	—	—	—	—	—	—

absorption was greatest from solutions of low pH.   Moreover, it was observed that the regulation of the hydrogen-ion concentration had a marked effect on the colour fastness.

Hydrogen-ion concentration has an important influence on the colours produced by various dyestuffs.   Holmes and Berliner (*Amer. Dyestuffs Reporter*, 1927, **16**, 81) have investigated the colours set up in different buffer solutions of known pH values, and have compiled a colour chart for use in the identification of dyes by the colours they give at different pH values.

In all probability, pH control will find a place in the manufacture of azo-dyes, and also in dyeing processes in which they are developed on the fibre by diazotising and coupling.   It is known that the hydrogen-ion concentration of the coupling bath is an important factor in the control of coupling, as it provides a method which materially assists in the reproduction of desired shades of colour and also in effecting a more complete coupling of the components.   Cellulose acetate silk enters into combination with organic bases, *e.g.*, paranitraniline, benzidine, etc. , which are diazotised on the fibre and then coupled with suitable naphthols and phenols to give various colours.   After converting the dyestuffs into water-soluble hydrochlorides, the baths are neutralised with sodium hydroxide so as to liberate the free dye base in colloidal suspension, some of which becomes fixed by the fibre.   When the hydrochlorides alone are used, not only are the colours different, but the dye is usually badly fixed to the fibre. pH control of the neutralisation should result in the production of more satisfactory dyeing.   The application of these dyes to

cotton, for which the process is reversed by first soaking the cotton in the hydroxy-compound, lends itself to pH control.

As equilibria between acids and bases play a part in the application to acetate silk of the "dispersol dyes" and the S.R.A. dyes (in which water-insoluble basic dyes are dissolved in concentrated Sulpho-Ricinoleic Acid, or highly sulphonated castor oil), it is likely that the hydrogen-ion concentration of the dyebath is a factor of some importance, both as regards the dye fixation and the possible deleterious effects of the acetate silk caused by hydrolysis through having too high a pH. The latter factor may arise in the laundering of acetate silk through the use of too alkaline a soap.

Potentiometric Methods for the Determination of Free Acid and Free Alkali in Dyestuffs.

Volumetric methods of estimating the acidity or alkalinity of dyestuffs are, of course, usually impossible. Callan and Horrobin
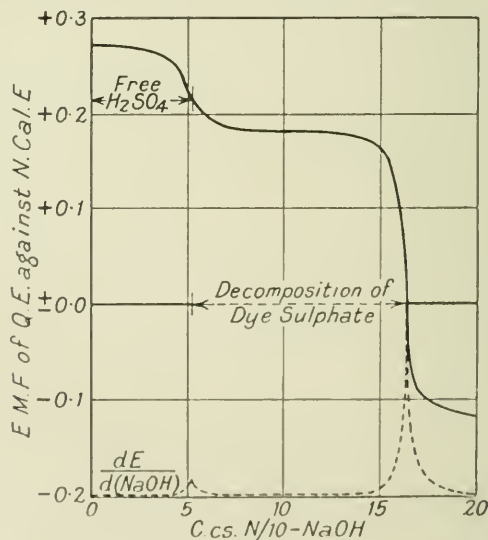
FIG. 108.—Quinhydrone Electrode Titration of a Dyestuff.

(*J. Soc. Chem. Ind.*, 1928, **47**, 332 T) have found the quinhydrone electrode to be especially useful in finding the sodium carbonate content of Congo-red, Benzo-purpurine, Milling Yellow, Orange I, Rhodamine, and Brilliant Orange ; their results being in excellent agreement with those obtained by purely chemical methods.

Since the quinhydrone electrode cannot be used in alkaline solution, they add a known amount of standard acid to a solution of a weighed amount of dyestuff, and after the carbon dioxide has been expelled by boiling, the cooled solution is titrated in the manner described on page 58. They find the method to be particularly applicable to the determination of acid in dye- stuffs and in dye-liquors, and to the detection of " free " acid in basic dyestuffs such as brilliant green, which is a hydro- chloride or sulphate of a colour base. Fig. 108 gives a quin- hydrone electrode titration curve of Brilliant Green sulphate, from which it will be seen that the amounts of free and combined sulphuric acid can be readily obtained.

CHAPTER XXXIII.

ORE FLOTATION.

CONSIDERABLE advances have recently been made in the development of flotation methods for the separation of ores from foreign matter, and also for the separation of one ore from another. The latter process is known as either differential, preferential, or selective flotation. After the minerals have been suitably ground, they are allowed to pass into a circuit of flowing liquid upon which some of the lighter and finely divided ores float, whereas the heavier and coarser particles sink. These methods have been extremely useful in ore concentration, especially in connexion with the sulphide ores, which when in similar states of subdivision are able to float to about the same extent. Notwithstanding this, it is very often possible to add some substance to the flotation medium that will cause the sulphide of some particular metal to sink. Thus at Cananea, Mexico (Tye, *Amer. Inst. Min. Met. Eng.*, 1927, Tech. Pub., No. 3) copper is extracted from a mineral, comprising chiefly chalcocite with some copper pyrites associated with iron pyrites in a siliceous gangue high in alumina, first by depressing the iron pyrites in alkaline circuit by means of as little as 0·08 lb. of xanthate per ton of ore. The concentrate contains only 4·6 per cent. of silica, which eliminates the need for roasting, and the concentrates are consequently placed in the reverberatory furnace. Because of the economic advantages accruing from these methods, their rate of development has been much greater than that of the chemistry and physics underlying them. The amounts of depressants to be added require careful control, and owing to the many and variable factors involved, such control is far from easy. When a satisfactory means of control has been devised, then it will be possible to obtain cleaner separations. Thus a varying proportion in an ore of the amount of a sulphide to be depressed will necessitate corresponding variations in the concentration of depressing agent in the flotation cells.

The mechanism of flotation is linked up with the operation of surface reactions, and therefore involves the following factors : size of particle, the angles of contact made between the particles

and the liquid surface, the surface tension of the medium, adsorption at the surfaces of the particles, and the tendencies of the particles to flocculate. Usually, the flotation medium is a mixture of water and oil. Flotation oils are both polar and non-polar. The former contain either alcohol or carboxyl groups which tend to make the oils soluble in water, and in the case of insoluble oils, to form extensive oil films on the surface of the water. This solubility influence of the polar groups becomes less and less as the chain of -CH_2 groups becomes longer. Hydrocarbons, and therefore containing no polar groups, have only very slight or no solubility, and spread on water to very small extents.

Almost all derivatives of the paraffins and the aromatic compounds (*e.g.*, alcohols, aldehydes, and acids) lower the surface tension of water, and for this reason on dissolving in water they tend to concentrate in the surface layer. With insoluble oils containing polar groups the tendency to dissolve rests in the polar groups, and as Langmuir (*J. Amer. Chem. Soc.*, 1917, **39**, 1849) showed, in the surface layer of oil on water the polar groups arrange themselves in direct contact with the water surface, leaving the non-polar or inactive groups to find the remote positions. This tendency to dissolve results in a lowered surface tension, and moreover, through the possible supersaturation of the surface layer of the water, in the formation of foam. A non-polar oil, on account of its inability to diminish the surface tension, is not adsorbed in the surface layer, and therefore accumulates on the surface in lenticular globules.

It has been pointed out that oils become adsorbed by minerals with their polar ends drawn into immediate contact with the surfaces, so that their inactive non-polar ends are outermost and thus come into contact with the flotation medium. Provided the particle were sufficiently small, this non-polar coating would tend to keep the oil-coated particle (as is the case with a globule of non-polar oil), floating on the surface of the liquid by virtue of its surface tension. Any diminution in the magnitude of the surface tension of the liquid might cause the particle to sink.

Now Langmuir has found that films of various fatty acids, alcohols, and esters are extraordinarily sensitive to very small amounts of acid, but not to salts in any great measure. N. K. Adam (*Proc. Roy. Soc.*, 1921, **99**A, 336) confirmed these results for palmitic acid, and furthermore found that the properties of the oil film on the surface of the water underwent variation with change in hydrogen-ion concentration. Though the films are insoluble in acid solution they become increasingly soluble with increasing pH, through the formation of salts. It will be seen therefrom

that the pH of the medium may be expected to have an important effect on its surface tension, and therefore upon its ability to float mineral particles.

Substances used as flotation promoters and depressants materially affect the hydrogen-ion concentration. To cause flotation of a mineral, acids are often employed, *e.g.*, sulphuric acid. Other substances used in flotation work are sodium carbonate, disodium phosphate, sodium cyanide, potassium bichromate, and copper sulphate. In differential flotation disodium phosphate is extensively used. Mineral suspensions appear to increase in stability in solutions having a pH greater than 7, and to show a tendency to flocculate in acid media. Fahrenwald (*Trans. Amer. Inst. Min. Eng.*, 1924, **70,** 647) states that in general, hydrogen-ion concentration appears to be *the* important factor in regard to the magnitude and sign of an electric charge on mineral suspensions. Sufficient has been written to indicate the possibilities of hydrogen-ion concentration control, though control will also depend upon many other factors inherent in flotation processes. For further information, the reader is referred to Technical Publications, Nos. 3 to 5, of the American Institution of Mining Engineers, 1927.

CHAPTER XXXIV.

MISCELLANEOUS INDUSTRIES.

Manufacture of Sweets.

THE character of syrups used in the confectionery industry is
partly determined by the hydrogen-ion concentration during the
boiling process, inasmuch as it is a factor on which the activity
of invertase depends. The optimum pH value is about 4·5,
a point that should be considered in the production of golden
syrup, corn syrup, cane and sorghum syrup, and maple syrup.
The inversion of cane sugar during boiling is proportional to the
hydrogen-ion concentration. If the extent of inversion has been
too great the syrup will be unsuitable for making into hard sweets.
Advantage is taken of the action of invertase in preparing fondants
and the creams, whose consistencies are the direct result of the
proportion of glucose formed. It is probable that pH measure-
ments would furnish a method of control.

Preservation and Canning of Food Products.

In order to preserve grain from possible diastatic action on the
starch from split grains, Legendre (*Comp. rend.*, 1927, **185,** 1156)
recommends the addition of small quantities of alkali materials to
raise the pH. The absence of sugars caused thereby prevents
further bacterial action, and so eliminates the usual rise in tem-
perature during the storage of grain with the attendant troubles
of germination and fermentation.

In the pasteurisation of fruit juices, yeasts and moulds must
be destroyed though the destruction of many kinds of bacteria
is unnecessary. Two points must be considered : (1) the lethal
rate of the destructive micro-organisms, and (2) the rate of the
penetration of heat. In the destruction of micro-organisms the
pH value is of vital importance, though this varies in the case
of different bacilli. Notwithstanding this, it is highly desirable
to maintain in canned fruit a pH value equal to that in the ripe
fruit in view of the possible influence on the taste that may be intro-
duced by a variation of this factor. Other difficulties arise in
canning through corrosion caused by the natural acidity of the
products. The pH of fruits lie below 4, tomatoes about pH 4·2,

vegetables usually between pH 5 and 6, and protein foods, *e.g.*, peas, fish, and meat, between pH 6 and 7 (*cf. National Canners Assoc., U.S.A., Bull.* 17L).

Manufacture of Fruit Jellies.

Valuable work has been carried out by Myers and Baker at the Delaware Agriculture Experimental Station (*Bulls. Nos.* 141 and 144, 1926) on the effect of the pH values of fruit juices used in the manufacture of jellies. At pH's above pH 3·50 to 3·55 it was not possible to prepare jellies. The most suitable pH range for the preparation of jellies appears to be from pH 2·85 to 3·30, the precise reaction depending on the nature of the acid used and the salts present.

Photography.

The many papers which have been published by Sheppard and his collaborators of the Kodak laboratories during the last few years emphasise the value of pH control. Thus hydrogen-ion concentrations have an important effect in the formation of emulsions and on the size of the silver halide particles dispersed within them. The tanning action, or " hardening," of aluminium or chromium salts on the gelatin emulsion is dependent upon acidity, as was shown to be the case in leather manufacture (p. 387). Neutral salts also exercise a temporary " hardening " action, and this likewise is a function of pH. Undue swelling of the gelatin film is prevented by the use of such solutions which, through their " buffer action," maintain a suitable range of pH. Another point in connexion with the ampholytic nature of gelatin is that unless its pH value is controlled the film may, in undergoing hydrolysis, cause the reduction of the silver salts. The reducing action of organic developers, *e.g.*, hydroquinone, is determined, not only by their concentrations in the reduced and oxidised forms, but by the hydrogen-ion concentrations (*cf.* p. 19). The reactions of agents employed in sensitisation, and especially of certain dyes, used for compensating optical defects, are influenced by the prevailing pH. Another point of interest concerns the " hypo " fixing bath. If the pH of the bath falls below about 3·5, the thiosulphate decomposes with the separation of finely divided sulphur, whereas if any iron compounds be present they will undergo precipitation with the production of stains when the pH exceeds about 5·5.

Emulsions.

Emulsification of oil-water mixtures is often effected in the presence of emulsifying agents, such as gums and soaps, and the

emulsions so formed are stabilised by the inclusion of small pro-
portions of acid or alkali. The stabilising action is probably due
to the chemical combination which takes place with the emulsifier,
and, the effect which this combination has in reducing the inter-
facial tension at the oil-water surfaces. In the past, there has
been a tendency to attribute variations in the stability of an emul-
sion to specific ions, and to overlook the fact that the salt solutions
containing these ions may have materially altered the pH of the
emulsion.

Krantz and Gordon (*J. Amer. Pharm. Assoc.*, 1926, **15**, 83)
prepared 25 per cent. emulsions of cotton-seed oil and water and of
heavy mineral oil and water, using acacia and tragacanth as emulsi-
fiers, and studied the effects on their stability introduced by vari-
ations in pH values by adding different amounts of sodium hy-
droxide and hydrochloric acid. The range of greatest stability
for either the emulsions of vegetable or mineral oils prepared with
acacia lay between pH 2 and 10, whereas using tragacanth, the
emulsions were only stable over the range pH 1·9 to 2·3. The size
of the particles in the acacia emulsions were far more uniform
and smaller than those in the tragacanth emulsions, and with the
former there was a slight increase in the particle size on both the
acid and alkaline side of the pH range, due to coalescence pre-
liminary to actual separation. The tragacanth emulsions were
especially stable within the narrow pH range indicated, but
quickly separated at higher pH values. The formation of water-
in-oil emulsions with the aid of magnesium oleate was found to be
more satisfactory in the case of olive oil than of mineral oil. The
pH range of maximum stability was from 11 to 12·5, and when
the pH sank below 2·5 extreme instability was produced (see
Colloid Symposium Monograph, VI., 1928, pp. 173 to 206).

Soap and Bath Salts.

Ordinary soaps impart to water a pronounced alkaline reaction,
varying as a rule from about pH 10 to pH 11·5. This high pH
accounts for the precipitating action of soap on the magnesium
and calcium salts contained in the water.

It is due to such high pH's that soaps have sometimes an ir-
ritating effect on the skin, through their solvent action on the
natural fatty sebaceous secretions deposited on the skin and so
rob it of its protective layer. Nevertheless, it is necessary to
remove the matter deposited in the pores from the sweat glands.
Among the substances used as bath salts are sodium carbonate,
borax and disodium phosphate, of which the first sets up the highest

pH and the last the lowest. Except for its slower rate of dissolution, borax has advantages in that it produces a pH value of about 9, which undergoes very little change with dilution, and does not precipitate as much of the salts as does sodium phosphate.

The pH of borax solutions varying from 0·2 to 9 per cent. ranges from 9·2 to 9·3 at 18°, and from pH 8·9 to 9·0 at 60° C. Borax, when used with a good quality soap considerably reduces the alkalinity of the soap. Thus at 38° to 40° C., a 0·5 per cent. borax solution had a pH value of 9·1, whereas a 5 per cent. toilet soap solution had a pH value of 10·3, yet the same amount of soap dissolved in a 0·5 per cent. borax solution yielded a solution of pH 8·8.

Dentifrices.

It is likely that the hydrogen-ion concentration of dentifrices is a factor which merits attention, for below pH 5·5 calcium phosphate becomes soluble, and thus it may be that any toothpaste of a low pH remaining in the crevices may be particularly destructive. Maclean (*Proc. Roy. Soc. Med., Sect. Odont.*, 1927, **20,** 873) experimenting on the possible initiation of caries by acid forming bacteria when grown *in vitro* in presence of teeth, found that unless an acidity of pH 5, or greater, is attained penetration of the enamel is very slow.

Petroleum Products.

Petroleum oils develop acidity when used in turbines, transformers, and oil-circuit breakers. It is a question of some importance to have a method by which the rate of acid production may be measured, as it supplies an indication of their stability. The usual method of determining the neutralisation number is to titrate an alcohol-water mixture containing a known weight of the oil either in the cold or after boiling with aqueous potassium hydroxide to a permanent pink with phenol-phthalein. The great objection to this method is the fact that the end-point is often obscured by the dark colour of the oil, or by the oil having formed an emulsion.

Two electrometric methods have been described; using (1) platinum electrodes only, and (2) platinum electrodes with quinhydrone. In the former method the titration cell is connected up thus :

| Pt | Alcohol - benzene neutralised to phenol-phthalein. | Saturated KI solution in agar-agar. | 10 gms. oil in 150 c.c. of alcohol-benzene containing KI. | Pt. |

The oil in the right-hand electrode compartment is titrated with
alcoholic potassium hydroxide until the two platinum electrodes
acquire the same potential indicated by the absence of a current
through a galvanometer on depressing a tapping key (*Proc. Amer.
Soc. Testing Materials*, 1925, **25**, 282).

The use of quinhydrone in the latter method (Seltz and
McKinney, *Ind. Eng. Chem.*, 1928, **20**, 542), whilst not permitting
the calculation of pH values, leads to satisfactory titration curves
by plotting the observed voltages against the volume of alkali
added.   Amyl alcohol was found to be the most suitable solvent
for oil on account of its relatively high dissociating power, and
because it could be made highly conducting by dissolving lithium
chloride in it.   The reference half-electrode used was a platinum
electrode immersed in amyl alcohol to which quinhydrone had
been added.   The alkali used for titrating was potassium or
lithium hydroxide dissolved in amyl alcohol and the junction
liquid was lithium chloride in amyl alcohol containing agar which
had set.

Foams as Fire Extinguishers.

Foams are becoming of importance in combating fires and
especially oil fires.   The foam is formed by the interaction of
two solutions, one of which contains sodium bicarbonate and a
foaming agent, *e.g.*, glue, glucose, liquorice extract, saponin
extract, and the other solution containing aluminium sulphate,
sometimes with very small amounts of sulphuric acid (*cf.* Swift,
Ind. Eng. Chem., 1924, **16**, 580).   The foam produced by the
evolution of carbon dioxide will be rendered more stable if the
bubble walls, reinforced by the gelatinous aluminium hydroxide
precipitated within them, are not rapidly ruptured by the too
sudden production of gas.   As emphasised by Swift, " a good
foam must be produced in large volume, must be tenacious so as
to withstand mechanical abuse, must be fluid enough to flow freely
over a burning surface of oil, but stiff enough to adhere to a vertical
surface when used on other fires, and must not wilt rapidly when
exposed to the flames."   In the opinion of the author, the efficiency
of such foams rests on the pH value set up by the two solutions
on mixing, both in regard to the rate of gas evolution and to the
quality of the precipitated aluminium hydroxide, *i.e.*, if the pH
value of the mixed liquids exceeds pH 4·1 at which aluminium
hydroxide just begins to separate.

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